A NEW DTA APPROACH

FOR VERIFYING PRECIPITATE SOLVUS IN INCONEL ALLOY 718

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Abstract

Using differential thermal analysis (DTA) to determine solvus temperature of precipitated phases in a Nb-hardened superalloy, such as alloy 718, is relatively difficult. The precipitation reaction is not significantly pronounced, and the baseline of a DTA thermogram is not clearly defined. A new approach was employed in this study, which utilized a solution-treated Inconel alloy 718 as the reference instead of the conventional alumina. The samples for analysis were preaged at various temperatures to develop specific precipitate phases. The DTA thermograms showed a well-defined baseline because of similar alloy chemistry and heat capacity between the sample and the reference. The offset of thermal peaks associated with precipitate dissolution can be accurately determined.

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Introduction

Differential thermal analysis (DTA) has been successfully applied to superalloys to provide important information about transition temperatures in alloy system. This versatile instrument can determine liquidus, solidus, incipient melting temperature, as well as various precipitation reactions in different superalloys [1-3]. It has been a useful tool, supplemental to other microscopic techniques, for understanding and characterizing the metallurgy of superalloys.

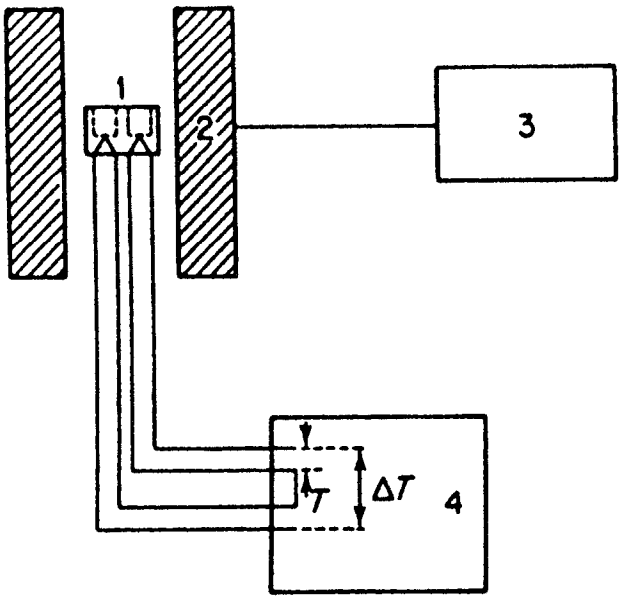
The application of DTA to Nb-hardened superalloys, like Inconel alloy 718, was limited to solid-liquid reactions, such as carbide or Laves-phase formation/dissolution and incipient melting [4,5]. Some successful work on the alloying effect of solidification segregation and tendency of Laves phase was performed recently by employing DTA. Very few attempts were made in the past to determine the temperature of solid-solid reactions such as precipitate solvus in Nb hardened superalloys. Precipitate solvus, below which the precipitate reaction takes place, is an important metallurgical information for metal processing and heat treatments to attain desirable properties.

The major difficulty using DTA to determine precipitate solvus in Inconel alloy 718 contributed by two unique features of precipitation in Nb-strengthened superalloys: low volume fraction and slow kinetics of precipitation. When the alloy contains sufficient Nb, the equilibrium secondary phase at aging temperatures is δ-Ni_3Nb, which has an orthorhombic (D0a) crystal structure. The precipitation of δ phase is highly heterogeneous because of the dissimilar structure with respect to the γ (fcc) matrix. The kinetics of δ precipitation is therefore slow, and the nucleation only occurs along grain boundaries. Themomechanical processing of alloy 718 is usually carried out at the temperature range that δ precipitation takes place. Large deformations during hot working may provide necessary nucleation sites for δ precipitation, and the dispersion of δ particles can serve as the pinning points to control the grain growth [6].

When alloy 718 is aged at low temperatures, some coherent precipitate will form homogeneously in the γ matrix. The major phase of coherent precipitates is designated as the γ'' phase, which has a body-centered-tetragonal ($D0_{22}$) ordered structure. The γ'' precipitates exhibit a large coherency strain along the tetragonal axis with the γ matrix. Consequently γ'' precipitates usually assume a disk morphology with three variants along cubic axes in γ matrix. The strengthening potential of γ'' precipitates is relatively high; it only requires a small volume fraction (<25%) to make alloy 718 a high strength superalloy. In spite of the homogeneous nature, the kinetics of γ'' precipitation is characterized as "sluggish" [7]. A certain incubation time will be observed upon aging before a significant hardening effect occurs. This sluggish nature of γ'' precipitation provides alloy 718 a better weldability than other superalloys.

There is a minor coherent precipitate phase, namely γ' (LI_2 ordered), which is commonly observed in other superalloys strengthened by Al and Ti. The volume fraction of γ' precipitates in alloy 718 is less than 5%.

Low volume fractions and slow precipitation kinetics would explain the difficulty of applying DTA to alloy 718. Extreme sensitivity is required to detect these low energy solid-solid precipitation reactions. This work reports a novel method to improve the accuracy of DTA through fundamental understanding of DTA principle. As the baseline of a DTA thermogram can be determined without ambiguity, the peak of a modest reaction can then be identified precisely. This approach was applied to the precipitations of δ, γ'', γ' phases to identify their solvus temperatures.



1. Sample/reference holder;
2. Furnace;
3. Temperature programmer;
4. Recording system.

Figure 1 - Block diagram of DTA apparatus

New DTA Approach

Figure 1 shows a block diagram of a typical differential thermal analysis (DTA) apparatus, consisting of several important components: 1. sample/reference holder; 2. furnace; 3. temperature programmer; 4. recording system. DTA measures the difference in temperature between a sample and reference which are exposed to the same heating (or cooling) schedule via symmetric placement with respect to the furnace. Both sample and reference rest on top of individual thermocouple pedestals. The reference must be an inert material that does not undergo any phase transition in the temperature range of interest. In case of superalloys, alumina is usually selected as the reference. The furnace surrounding both sample and reference offers a steady heating rate, and the temperature difference between sample and reference is plotted against time, or in practice, against the temperature.

Any phase transition occurring to the sample which involves the evolution of heat will cause its temperature to raise temporarily above that of reference, thus giving rise to an exothermic peak on the DTA thermogram. An exothermic peak shows at the solidification or the precipitation of a phase in a superalloy. Conversely, a phase transition which is accompanied by the absorption of heat will cause the sample temperature to lag behind that of reference, leading to an endothermic peak. Examples in superalloys are incipient melting and dissolution of precipitate phases.

Ideally the heat capacities of both sample and reference are constant, and the heating of the furnace is uniform. The measured temperature difference, ΔT, is a linear function of temperature, which is designated as the baseline. A perfect baseline is horizontal line with a small and steady ΔT.

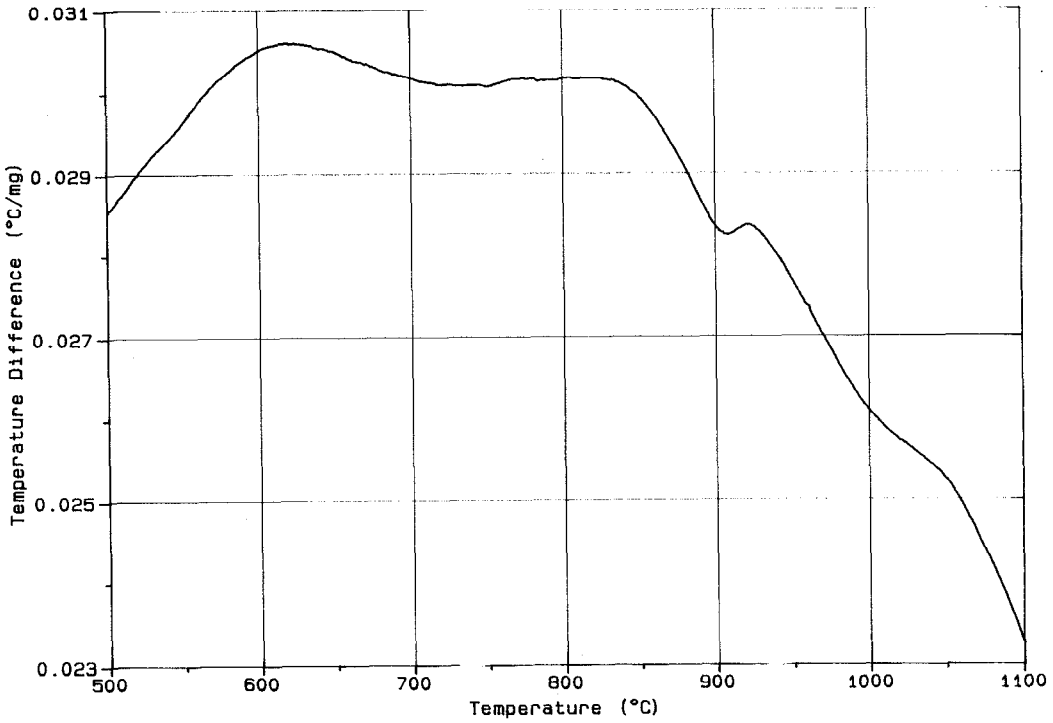


Figure 2 - DTA thermogram of alloy 718 annealed at 1050°C

The ideal case of a perfect baseline seldom occurs in practice by conventional DTA practice. There are many factors, such as sample mass and packing density of reference powder, causing the baseline to deviate from a horizontal line. The main reason of deviation is contributed to the difference in the heat capacity and thermal conductivity between the sample (superalloy) and the reference (alumina). Figure 2 shows a typical DTA thermogram of heat-treated alloy 718 using alumina as the reference. Temperature difference between sample and reference increases with temperature; the rate of change is not constant but varies with temperature . The baseline can not be defined precisely, and the offset temperatures of a reaction peak are difficult to decide accurately.

The new approach proposed in this work is to compare DTA between two samples with the same alloy composition but different microstructure. In case of alloy 718, the reference will be an alloy 718 containing no precipitate, and the sample will be a heat-treated alloy 718 with some specific precipitates. Both heat capacity and thermal conductivity between the sample (alloy 718 with precipitate) and the reference (alloy 718 without precipitate) would be very similar. Hopefully the ideal baseline can be attained. The reaction peak in the thermogram, which is associated with the dissolution of precipitates in the sample, can be well defined. As a result, the precipitate solvus corresponding to the end of the dissolution peak can be determined accurately.

Experimentals

Materials

A segment of alloy 718 bar was obtained from the commercial production line. The heat was prepared through standard wrought alloy 718 procedures, and the analyzed chemistry satisfied the commercial specification. Table I list the chemical composition of alloy 718 material used in this study. The bar received the final heat treatments, as shown in Table I, including solution anneal and double aging.

Table I. Chemical Composition (wt. %) and Heat Treatment of Alloy 718

Element	Analyzed	Specification
Ni	53.46	50.0-55.0
Cr	18.65	17.0-21.0
Fe	Balance	Balance
Mo	3.06	2.80-3.30
Nb	5.08	4.75-5.50
Ti	0.99	0.65-1.15
Al	0.72	0.20-0.80
C	0.035	0.08 max

Heat Treatments solution anneal: 955°C/1hr, air cool.
double aging: 720°C/8hr, furnace cool at 50°C/hr to 620°C/8hr, air cool.

The T-T-T diagram of alloy 718 is given in Figure 3 [8]. The precipitation reaction of interest in this work were: the equilibrium phase, δ-Ni_3Nb and the coherent precipitates, γ″ and γ′. As seen in Figure 3, the ratio of precipitate hardening elements, Ti + Al/Nb, may affect the amount and solvus of coherent precipitates. New DTA approach suggested in this work offers an effective and efficient method to characterize this alloying effect.

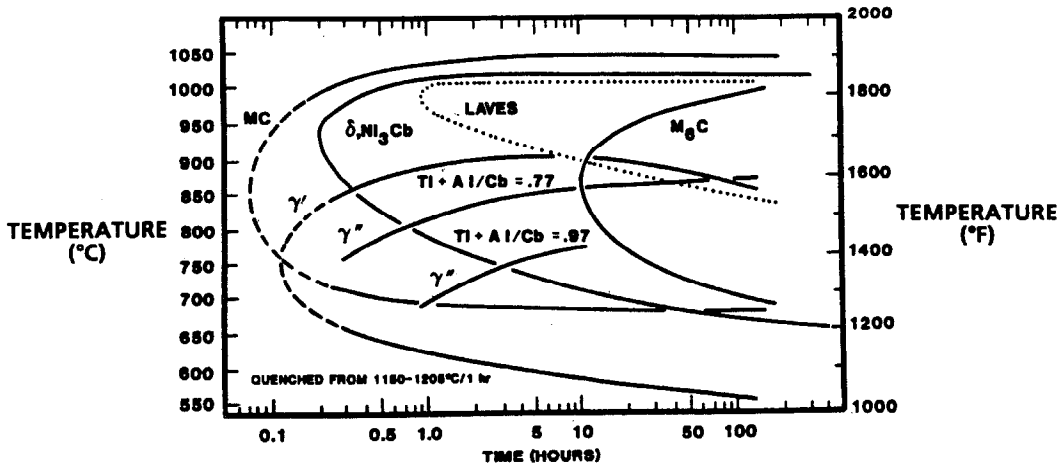


Figure 3 T-T-T Diagram of Alloy 718

The material of alloy 718 in this study was solution treated at 1050°C for one hour followed by water quench. This heat treatment would dissolve all intermetallic precipitates (δ, γ', γ'') and generated a "clean" microstructure with no precipitate. This condition was used as the reference in the DTA runs.

To develop different precipitates, different samples of solution treated alloy 718 were given specific heating treatments, respectively.

- 900°C/4 hr for δ precipitates;
- 800°C/8 hr for γ' precipitates;
- 700°C/16 hr for γ'' precipitates.

DTA Procedures

DTA tests were performed on the above samples; both conventional and new approaches were used. Typical sample size was 150 to 200 mg. The heating rate was 40°C/min. To prevent oxidation, a free flow of high purity helium was applied at a flow rate of 100 cc/min.

Metallography

Metallography was performed on all the specimens heat treated as mentioned above. Samples were mounted and polished through the standard laboratory procedures to 0.03 um alumina and then etched in 7 acid (a mixture of seven acids) solution for a specific time necessary to reveal the structure of interest at room temperature.

Hardness Test

Bulk hardness was performed on a Rockwell hardness test machine. The major load is 100 kg for Rockwell B and 150 kg for Rockwell C. The minor load is 10 kg for both of them. Brale diamond indenter was used in Rockwell C and steel ball is adopted in Rockwell B.

The samples were cut into the dimension of 1cm×1cm×2cm, two surfaces of 1cm×1cm were polished through grit 320 sand paper to make them flat and parallel to each other. Hardness was first measured on Rockwell scale. If the measured R_C is less than 25, then it was measured again on Rockwell B scale to make the results more accurate.

Results

Metallography and Hardness

Microstructures of alloy 718 samples prepared in this study were examined by optical microscopy. Figures 4(a) to 4(d) show the metallography of each sample after the designed heat treatment. Solution treated at 1050°C generated a fully recrystallized, equiaxed grain structure. The grain size was measured to be 35 um. All intermetallic precipitates were dissolved after this heat treatment and remained a clean fcc matrix with a supersaturated solid solution of precipitation elements.

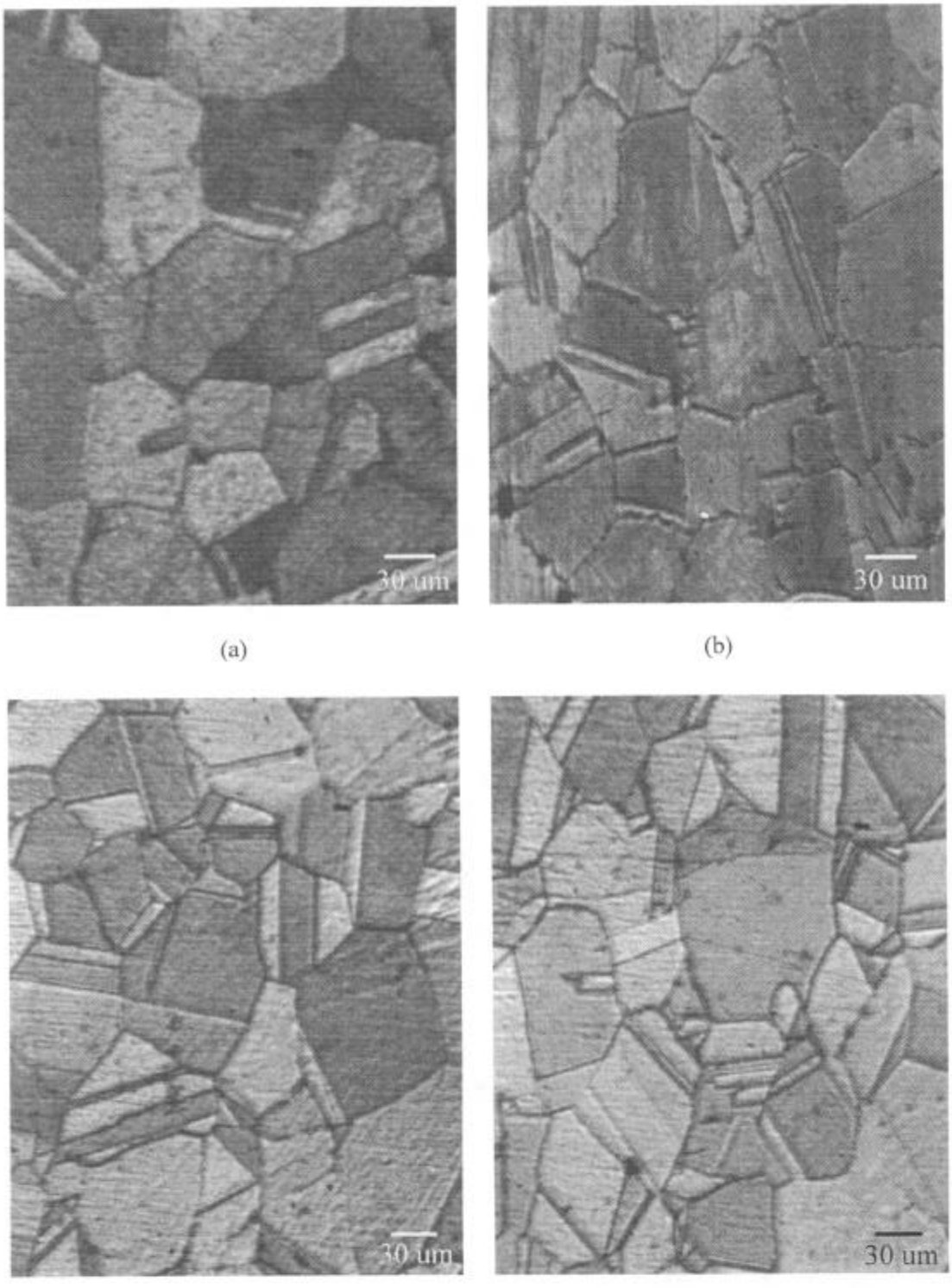


Figure 4 - Microstructure of alloy 718 (a) solution annealed at 1050°C/1hr; (b) aged at 900°C/4hr; (c) aged at 800°C/8hr; (d) aged at 700°C/16hr

Precipitation of δ-Ni_3Nb was evident when alloy 718 was subjected to 900°C. Figure 4(b) shows clearly the heterogeneous nature of δ precipitation, which has a plate-like morphology. The plates were aligned on specific crystallography plane, i.e., {1 1 1}, in each grain. The nucleation of δ plates occurred primarily along grain boundaries; occasionally some δ plates formed inside grains.

Samples aged at 800°C and 700°C had a similar microstructure as that of solution treated one under optical microscopy. As proved by hardness results, the coherent precipitates were developed in both cases. Therefore, the precipitate size would be smaller than the resolution of microscopy in the sub-micron scale.

Rockwell hardness tests were conducted to confirm the precipitation reactions and to evaluate the age hardening effects. The average hardness and the standard deviation of five measurements on each sample are given in Table II. The hardness scale was changed from R_B to R_C when the sample had a pronounced hardening response by heat treatment.

Table II. Hardening of Inconel Alloy 718 by Different Heat Treatments

Heat Treatments	Major Precipitate	Rockwell Hardness	Standard Deviation
1050°C/1hr	none	R_B 82.8	± 0.2
900°C/4hr	δ-Ni_3Nb	R_B 91.7	± 0.8
800°C/8hr	γ′	R_C 36.4	± 0.3
700°C/16hr	γ″	R_C 37.3	± 0.5

All heat treatments for different precipitations at individual temperatures resulted in a definite age hardening. Low-temperature aging at 800°C and 700°C caused a significant hardness increase in alloy 718 because coherent γ′ and γ″ precipitation occurred. It was difficult to separate two coherent precipitates by alternating the aging temperature. Based on their coherency nature, the γ′ precipitates were expected to form extensively at 800°C aging, although some γ″ precipitates might also appear. At 700°C, the precipitation was dominated by γ″ coupled with a small amount of γ′. A higher hardness observed at 700°C aging was contributed partly by a better strengthening effect of γ″ precipitates and partly by the more supersaturation of precipitation elements.

A small but confirmed hardening was observed at 900°C aging, at which heterogeneous δ precipitates were expected to develop. As shown in Figure 4(b), δ precipitation occurred predominantly along grain boundaries. These large plate-like precipitates did not cause as pronounced hardening as the coherent precipitates.

DTA of Heterogeneous Precipitation

The difference in crystal structure and lattice constant between δ phase and γ matrix causes the heterogeneous nucleation of δ precipitates. The precipitation reaction is slow kinetically and requires a high-temperature aging to overcome thermal activation energy. Alloy 718 aged at 900 °C showed the formation of δ precipitates. The aged sample was used to run DTA tests

using aluminum as the reference. The resultant DTA thermogram is plotted in Figure 5. The reaction peak associated with the dissolution of δ precipitates was hard to detect. In addition, the baseline in this case is curved and difficult to be defined precisely. Therefore the offset of δ-dissolution peak is impossible to determine accurately.

A new approach suggested in this work employed the solution-treated alloy 718 as the reference for DTA run. Figure 6 shows the DTA thermogram of the sample aged at 900 °C using a reference of alloy 718 annealed at 1050 °C. The obvious difference observed in Figure 6 is the well-defined, linear baseline, which provided a clear advantage to determine the precipitate solvus from the DTA thermogram.

There are two reaction peaks observed in Figure 6. One peak appears at 948°C and the other at 853°C; both of them are endothermic suggesting the dissolution of precipitates. As δ precipitates were developed by aging at 900°C, the high temperature peak ought to correspond the dissolution of δ precipitates. The offset of this peak was determined to be 998°C. The second reaction peak at the low temperature is related to the coherent precipitation that will be discussed later.

DTA of Coherent Precipitations

Coherent precipitations in alloy 718 include γ′ and γ″, which co-exist at most temperatures. These homogeneously nucleated precipitates were relatively small which provided a significant strengthening effect. The kinetic of precipitation reaction was remarkably faster than those of incoherent precipitates like equilibrium δ phase. A pronounced peak was expected for the dissolution of coherent preciptates.

Figures 7 and 8 show DTA thermograms for the samples aged at 800°C and 700°C, respectively. Solution-treated alloy 718 was employed as the reference. In both cases, the linear baselines were obtained with the distinctive reaction peak. The solvus temperature for γ′ precipitates was measured as 960°C from the sample aged at 800°C. On the other hand, the γ″ solvus was measured as 894°C from the sample aged at 700°C. There was a reaction peak occurred at about 650°C; it is believed to be the coherent precipitation during the heating of DTA tests.

The T-T-T diagram of alloy 718 shown in Figure 3 suggests a flat top of the C-curve for δ precipitation. It is easy to define the solvus temperature from the C-curve of δ precipitates. However, the C-curves for coherent precipitates, γ′ and γ″, are more symmetric to their nose; the solvus temperatures are not clearly defined. The metallographic method to determine the solvus of coherent precipitates was hampered by their small sizes. The new approach of DTA method in this work provides one of the most efficient technique for measuring the solvus temperature of coherent precipitates.

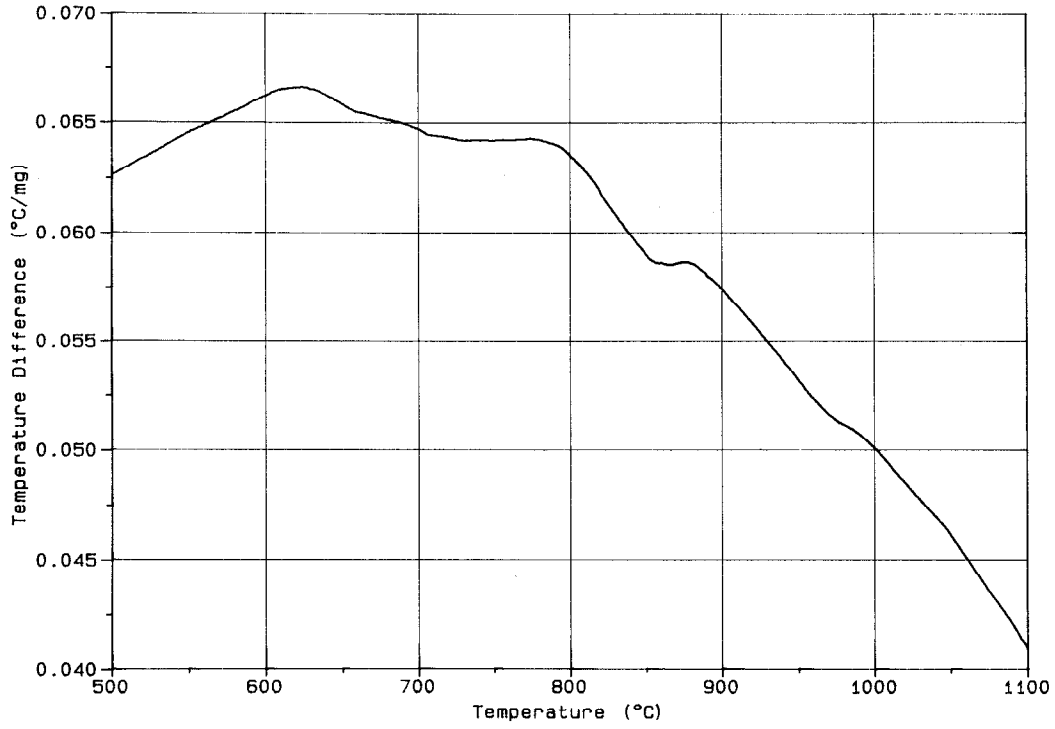


Figure 5 - DTA thermogram of Inconel 718 aged at 900°C using alumina as the reference

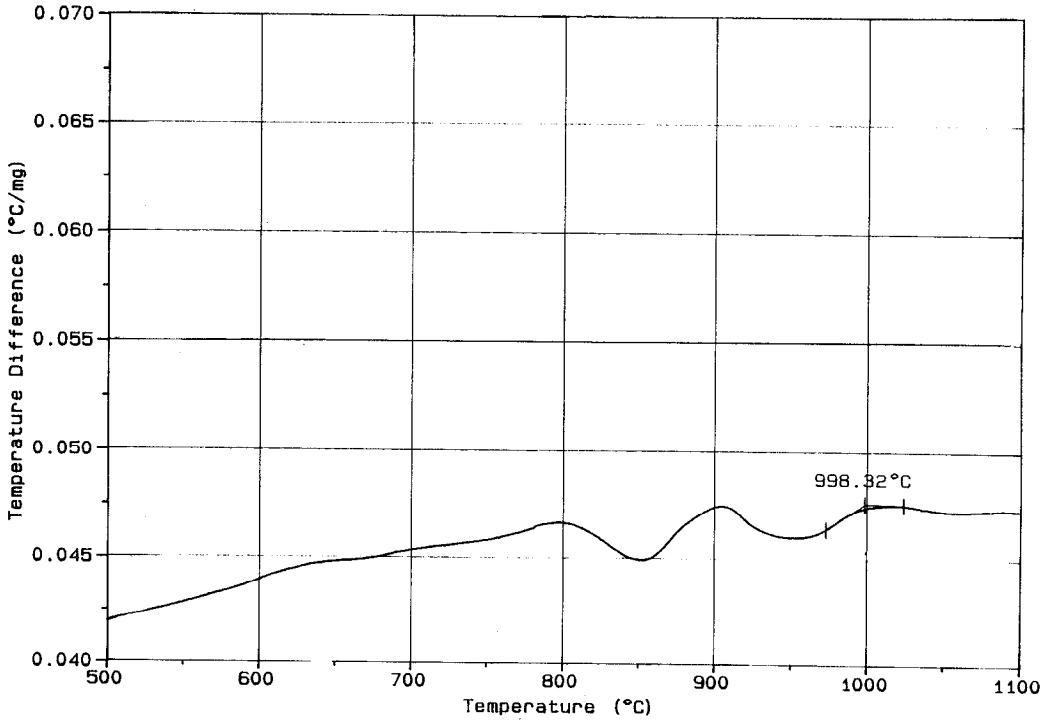


Figure 6 - DTA thermogram of Inconel 718 aged at 900°C using solutioned Inconel 718 as the reference

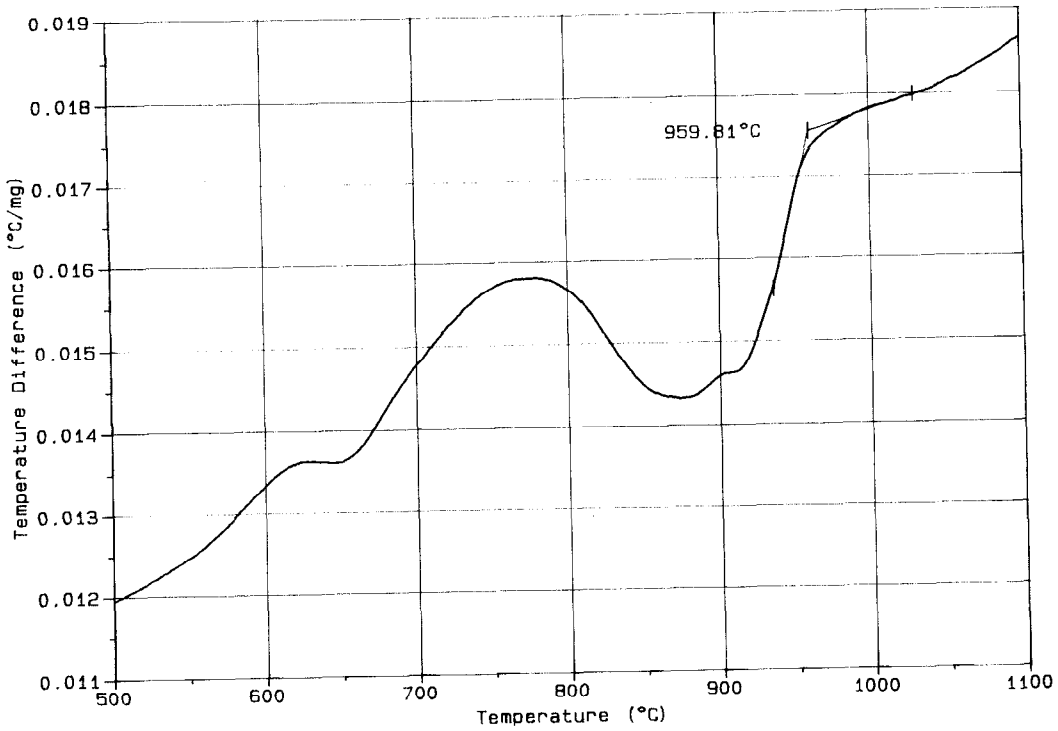


Figure 7 - DTA thermogram of Inconel 718 aged at 800°C using solutioned Inconel 718 as the reference

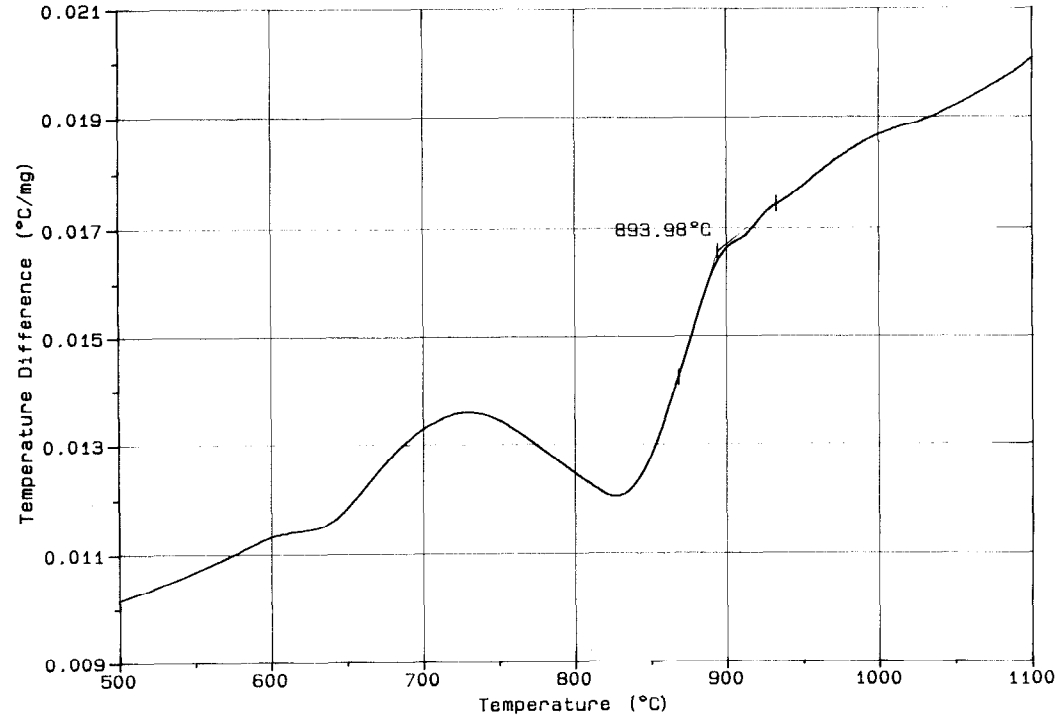


Figure 8 - DTA thermogram of Inconel 718 aged at 700°C using solutioned Inconel 718 as the reference

Discussion

Conventional DTA technique has been known to be an effective method for studying the liquid-solid phase transition in metals and alloys. The latent heat involved in liquid-solid reaction is generally great, and the kinetic of transition is instantly. A pronounced reaction peak can be detected on thermogram during either heating or cooling. The onset and offset temperatures of such a reaction would be determined straight forward. In contrast, the precipitation is a solid-solid reaction, which consists of the nucleation and the growth of precipitates. The nucleation rate depends on the degree of supersaturation; the lower the temperature is, the more supersaturation occurs. Theoretically there is only the offset temperature of precipitation reaction, which corresponds to the precipitate solvus. The onset temperature is simply a limitation of precipitate growth kinetic, which is thermally activated. It requires a certain temperature to activate precipitate growth rate to catch up the heating rate of DTA.

The new approach used in this work has two important differences from the conventional DTA method. The sample in the conventional DTA setup contains no precipitate initially, and the precipitation is expected to occur during the heating process. If precipitation kinetic is extremely slow, such as those incoherent precipitates, a small or even no reaction peak will appear on DTA thermogram. The new approach intentionally introduces a significant amount of precipitates in advance. The DTA test will focus on the dissolution of existing precipitates at high temperatures. The intensity of reaction peak would be intensified with favorable reaction kinetics.

Employing a solution-treated sample as the reference in the new approach eliminates the major difference in heat capacity and thermal conductivity. The consequent effect is the linear baseline of DTA thermogram, which is essential to determine accurately the offset of the reaction peak. However, this new approach can only be applied on the solid-solid reaction, but not on solid-liquid one.

One aspect of the new approach requires special caution to interpret the results. There is a possibility that some precipitation reaction occurs during the heating of a DTA test. Coherent precipitation may progress fast enough to be detected. In this case, the coherenct precipitation appears in both sample and reference, and a self compensation would occur. Nevertheless, an additional minor peak shows up as seen in Figures 7 and 8. Since the minor peak located at about 650°C, it is likely to be associated with the formation of γ'' precipitates in the reference.

Summary

A new DTA approach has been introduced to measure the solvus temperature of different precipitates in alloy 718 superalloy. Two major steps were adopted:

1. an aging treatment was applied in advance on the sample to form a substantial amount of precipitate, whose solvus temperature would be determined;
2. a solution-treated sample of the same alloy was employed as the reference.

The DTA thermogram made using this new approach showed a pronounced endothermic peak associated with the dissolution of precipitates in the sample. A linear baseline was obtained, and the offset of the reaction peak could be accurately determined. The new approach can used for the heterogeneous precipitation, δ-Ni_3Nb, as well as for the coherent precipitation, γ' or γ''.

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