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Short Communication

THERMOPHYSICAL PROPERTY DETERMINATION OF HIGH TEMPERATURE ALLOYS BY THERMAL ANALYSIS

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Abstract

Differential scanning calorimetric measurements to determine solidus and liquidus temperatures and latent heat of fusion of two high temperature materials, PWA1484 and an experimental gamma titanium aluminide alloy, are presented. The solidus and liquidus temperatures of PWA1484 are 1340 and 1404°C. The solidus and liquidus temperatures of the titanium aluminide alloy are 1453 and 1522°C. Solidus and liquidus temperatures determined from actual heating and cooling curves, which were measured using imbedded thermocouples and analyzed by a pseudo-differential thermal analysis technique are found to be in good agreement with the differential scanning calorimetric measurements.

Keywords: DSC, DTA, latent heat of fusion, melting, PWA1484, solidification, titanium aluminide

Introduction

Reliable knowledge of the thermophysical properties of materials is essential for the interpretation and the modelling of high temperature alloy solidification behaviour. To perform a coupled thermal-fluid flow analysis involving a phase change typically requires, as a minimum, thermal conductivity, density, specific heat, solidus and liquidus temperatures, latent heat of fusion, and viscosity. For some materials, such as steels, aluminum and copper alloys, and some superalloys, this data is available in handbooks or in the open literature. However, for newer alloys, such as titanium

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aluminide intermetallics and the latest generations of single crystal nickel-base superalloys, these thermophysical properties are not readily available. The lack of this data reflects the experimental complications encountered when working with such reactive alloys at high temperatures [1, 2].

Several thermal analysis techniques can be used to measure the required thermophysical properties [3–5]. Differential thermal analysis (DTA) allows the recognition of thermal effects including melting and solidification and other phase transitions. Thus, solidus and liquidus temperatures can be obtained. Differential scanning calorimetry (DSC) is useful for determining transformation energetics, such as the latent heat of fusion, and thermophysical properties, such as specific heat. Until recently, the maximum use temperature of DSC equipment was limited to temperatures below those of interest for high temperature alloys with melting temperatures in the range of 1200 to 1500°C. However, a newly developed high temperature differential calorimeter allows testing up to 1650°C [6]. Heating and cooling curves, measured during solidification using thermocouples imbedded in the melt, can also be used to deduce solidus and liquidus temperatures [7]. In this study, both DSC and analysis of heating/cooling curves were used to determine solidus and liquidus temperatures of two high temperature alloys: PWA1484 and an experimental gamma titanium aluminide alloy. DSC was also used to determine the latent heat of fusion of these alloys.

Experimental

The materials studied were PWA1484, a second-generation single crystal superalloy, and TAWS, an experimental gamma titanium aluminide alloy. The PWA1484 was supplied by PCC Airfoils Inc., Minerva, OH in the form of single crystal bars approximately 19 mm in diameter and 180 mm in length. The chemical composition of PWA1484, in mass percent, was Ni–4.82 Cr–1.89 Mo–5.83 W–2.91 Re–8.53 Ta–5.64 Al–10.11 Co–0.07 Hf. The TAWS alloy was supplied by Flowserve, Dayton, OH in the form of cast bars approximately 19 mm in diameter and 280 mm in length. The chemical composition of TAWS, in atomic percent, was Ti–48 Al–2 W–0.5 Si. For the DSC measurements, small samples were cut from the as-received material having masses of 86.37 mg (PWA1484) and 23.29 mg (TAWS). The samples were then cleaned ultrasonically and rinsed in acetone and methanol. For the heating/cooling curve analysis, the as-received bars were cut to appropriate lengths. Longitudinal holes were drilled in the bars to accommodate thermocouples. The bars were subsequently ground to remove any surface reaction layers, cleaned ultrasonically, and rinsed in acetone and methanol.

DSC was performed using a Netzsch model DSC 404 C Pegasus capable of operation to 1650°C. Platinum crucibles with alumina liners and lids were used for the tests. The inner surface of the crucibles was coated with an yttria spray to avoid reaction between the sample and the alumina liner. The system was evacuated several times with a turbo molecular pump system and back-filled with high-purity argon prior to the tests. Testing was performed under a flowing argon atmosphere. The samples were heated and cooled between room temperature and 1520°C (PWA1484)/1560°C (TAWS) at heating and cooling rates of 20°C min^{-1}.

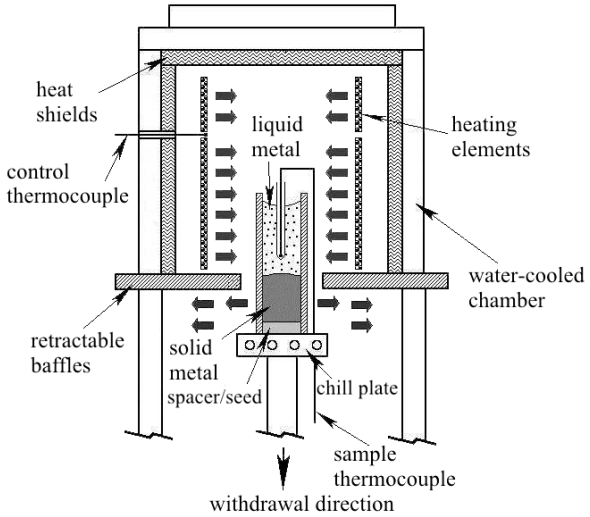

Fig. 1 Schematic of the Carleton University modified Bridgman furnace

Heating/cooling curves were generated in a modified Bridgman furnace. The furnace is described in detail in [8] and a schematic is shown in Fig. 1. High purity alumina tubes were used as molds for PWA1484 while yttria tubes were used for TAWS. A thermocouple, protected by a sheath of alumina (PWA1484) or yttria (TAWS) was placed in each sample to record the metal temperature during melting and re-solidification. The sample was placed on the copper chill plate and raised into the hot zone of the furnace. The furnace was evacuated twice and back-filled with high-purity argon prior to heating. Heating/cooling was performed under a positive pressure of flowing argon. The samples were heated at various rates until molten and then withdrawn, at various rates, into the cold zone of the furnace, thus re-solidifying the bar in a directional manner.

Results and discussion

The DSC heating and cooling results for PWA1484 are shown in Fig. 2. By comparing the DSC traces to those of various superalloys [9, 10] the peaks and transformation temperatures were identified. The phase transformation with peak temperatures of 1256°C (heating) and 1217°C (cooling) corresponds to the solutioning and precipitation of the gamma prime (γ') phase. The γ' solvus temperature ($T_{\gamma'}$) is 1320°C (extrapolated finish, on heating). On heating, the solidus (T_s) is 1340°C (extrapolated onset) and the liquidus (T_L) is 1404°C (peak). On cooling, the liquidus is 1373°C (extrapolated onset) and the solidus is 1297°C (extrapolated finish). The characteristic step/peak at 1358°C (heating) and 1310°C (cooling) corresponds to the melting and formation of the interdendritic γ–γ' eutectic. The transformation temperatures measured on heating are more representative of the 'true' values than those measured on cooling due to undercooling effects [11, 12]. Thus, for PWA1484 the γ' solvus is 1320°C, the solidus is 1340°C, and the liquidus is

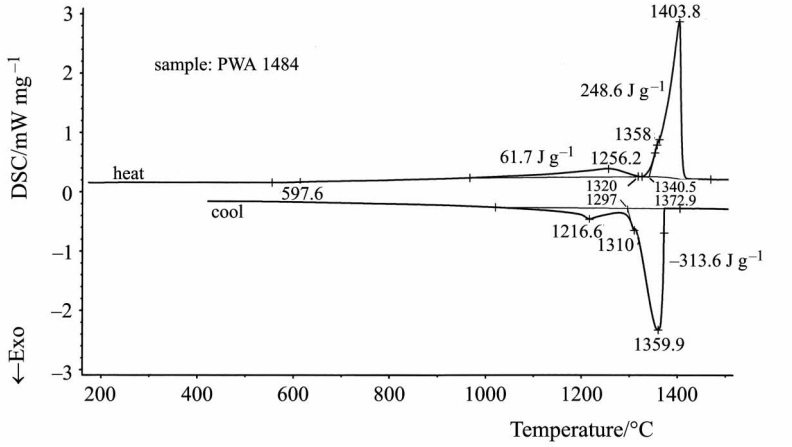

Fig. 2 DSC heating and cooling curves for PWA1484

1404°C. These correspond well to reported values: solidus of 1338°C [13] and liquidus of 1399°C [12]. Cetel and Duhl [13] reported a γ' solvus of 1299°C, but they also stated that some coarse as-cast γ' remained after a solution treatment of 1316°C for 4 h. Therefore, the true γ' solvus must be greater than 1316°C, which agrees with the current DSC-measured value of 1320°C. The latent heat of fusion, L_f, measured during melting, is 249 J g^{-1}. This is comparable to the value of 277 J g^{-1} reportedly used in the simulation of nickel-base superalloys [14].

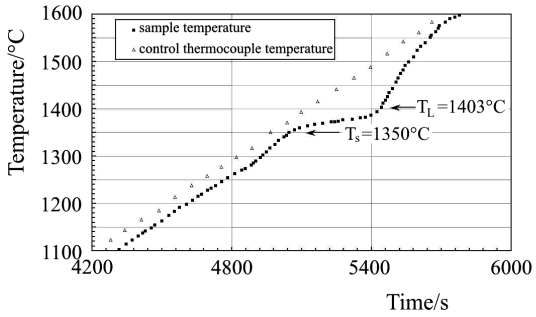

Fig. 3 Furnace control thermocouple and sample temperatures measured during heating of PWA1484

Heating and cooling curves for melting and re-solidification of PWA1484 are shown in Figs 3 and 4. The temperature arrest due to melting is clearly visible on the heating curve (Fig. 3), with approximate solidus and liquidus temperatures taken as 1350 and 1403°C. A 'pseudo-DTA' (p-DTA) analysis was performed using the heating curve. The difference between the furnace control and sample thermocouple temperatures was plotted *vs*. the sample temperature creating a DTA-like profile shown in Fig. 5. Solidus and liquidus temperatures are taken as 1350°C and 1403°C. Also evident is the solutioning of the γ' phase, with a γ' solvus of 1320°C. The transformation temperatures measured by p-DTA (γ' solvus of 1320°C, solidus of 1350°C, and

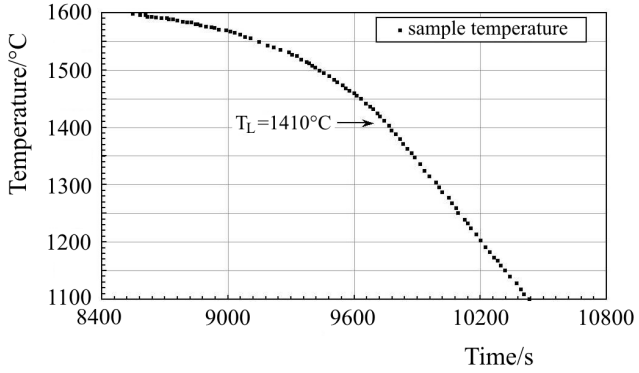

Fig. 4 Sample temperature measured during cooling of PWA1484

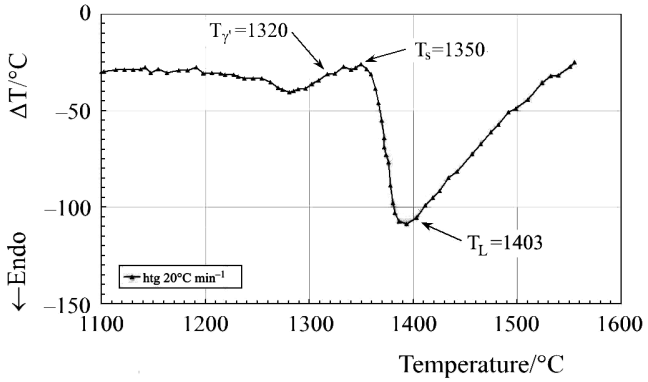

Fig. 5 DTA heating curve for PWA1484. Δ*T* is the difference between the furnace control thermocouple and sample temperatures and is plotted *vs*. the sample temperature

liquidus of 1403°C) correspond very well to those measured by DSC and to literature values. The break in the cooling curve (Fig. 4) at approximately 1410°C is taken as the liquidus temperature, and corresponds relatively well to the values measured by DSC and the p-DTA given that under these particular solidification conditions the break in the cooling curve is relatively poorly defined. Further cooling curve analyses (calculation of first and second derivatives of the cooling curve) could potentially better delineate the liquidus temperature. Minimal undercooling was exhibited during re-solidification in the Bridgman furnace because solidification occurred by re-growth of unmelted solid from the bottom of the sample.

The DSC heating and cooling results for TAWS are shown in Fig. 6. The physical metallurgy of gamma titanium aluminide alloys at high temperatures is still not well understood, especially for ternary and quaternary alloys such as this one. There is also limited thermal analysis data for these alloys reported in the literature. This makes the task of identifying the various transformation temperatures and phase transitions more difficult. On heating, the solidus is 1453°C (extrapolated onset) and the liquidus is 1522°C (extrapolated finish). Peak temperatures are measured at 1485 and

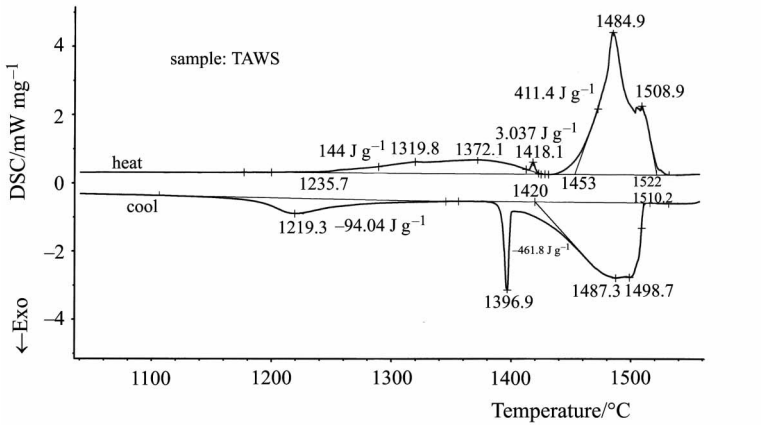

Fig. 6 DSC heating and cooling curves for TAWS

1509°C. On cooling, the liquidus is 1510°C (extrapolated onset) and the solidus is 1420°C (extrapolated finish). Characteristic peaks are measured at 1499 and 1487°C. The effects of undercooling on the solidus and liquidus temperatures are again evident. A terminal solidification event occurs at 1397°C (peak) and may correspond to the peritectic reaction or possibly to a solid state reaction. Further investigation is required to positively identify this reaction. The latent heat of fusion, measured during melting, is 411 J g^{-1}.

A pseudo-DTA analysis was also performed using temperature data from several TAWS samples at various heating rates and is shown in Fig. 7. The average solidus and liquidus temperatures are 1452 and 1511°C. It seems that this liquidus temperature corresponds to the peak temperature that was measured by DSC at 1509 and not the 1522°C extrapolated finish temperature. The average 'peak' temperature of 1480°C indicated on Fig. 7 most likely corresponds to the peak temperature that was measured by DSC at 1485°C. Again, the transformation temperatures measured by p-DTA closely match those measured by DSC.

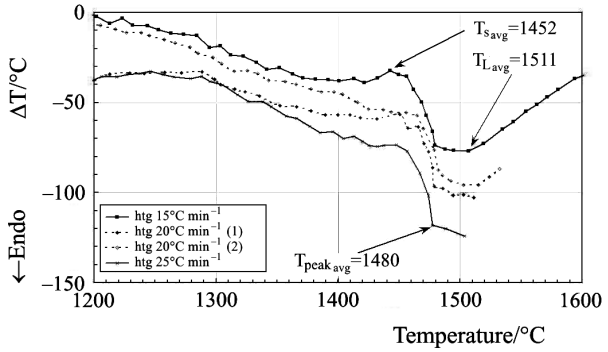

Fig. 7 DTA heating curves for TAWS. Δ*T* is the difference between the furnace control thermocouple and sample temperatures and is plotted *vs.* the sample temperature

Conclusions

DSC and p-DTA analyses have provided some of the thermophysical data necessary to simulate the solidification of PWA1484, a second-generation single crystal superalloy and TAWS, an experimental gamma titanium aluminide alloy. The data obtained by these techniques, as well as data available in the literature are summarized in Table 1. The values for solidus and liquidus temperatures and for latent heat of fusion are largely in agreement. Some discrepancies are certainly expected, especially with regard to the p-DTA measurements as they were made in an apparatus not typically used for thermal analysis. However, they were remarkably accurate considering the simplicity of the modified Bridgman furnace as a thermal analysis tool, as compared to a typical DTA instrument.

Table 1 Summary of measured and reported thermophysical properties

Alloy	Property	DSC	p-DTA	Reported value
PWA1484	T_s/°C	1340	1350	1338 [13]
	T_L/°C	1404	1403	1399 [12]
	T_γ	1320	1320	>1316 [13]
	L_f/J g^{-1}	249	–	277 [14]
TAWS	T_s/°C	1453	1452	–
	T_L/°C	1522	1511	–
	L_f/J g^{-1}	411	–	–

References

1 P. N. Quested, K. C. Mills, R. F. Brooks, B. Monaghan, A. T. Dinsdale, A. Day, M. J. Richardson, R. J. L. Andon, R. Taylor and H. Szelagowski, Modelling of Casting, Welding and Advanced Solidification Processes VII, The Minerals, Metals & Materials Society, Warrendale, PA 1995, p. 407.
2 R. F. Brooks, A. P. Day, K. C. Mills and P. N. Quested, Int. J. Thermophys., 18 (1997) 471.
3 M. I. Pope and M. D. Judd, Differential Thermal Analysis: A Guide to the Technique and its Applications, Heyden & Son Ltd., Bellmawr, NJ 1977.
4 G. Widmann and R. Riesen, Thermal Analysis: Terms, Methods, Applications, Dr. Alfred Huthig Verlag Heidelberg 1987.
5 M. E. Brown, Introduction to Thermal Analysis: Techniques and Applications, Chapman and Hall, New York NY 1988.
6 J. Blumm and E. Kaisersberger, J. Therm. Anal. Cal., 64 (2001) 385.
7 I.-S. Jung, M.-C. Kim, J.-H. Lee, M.-H. Oh and D.-M. Wee, Intermetallics, 7 (1999) 1247.
8 L. Zhao, D. Y. Seo, H. Saari, J. Beddoes and S. Durham, Canadian Aeronautics and Space J., 47 (2001) 222.
9 J. Lecomte-Bechers, Metall. Trans. A, 19A (1988) 2333.

10 J. S. Zhang, Z. Q. Hu, Y. Murata, M. Morinaga and N. Yukawa, Metall. Trans. A., 24A (1993) 2443.
11 M. J. Cieslak, T. J. Headley, G. A. Knorovsky, A. D. Romig, Jr. and T. Kollie, Metall. Trans. A., 21A (1990) 479.
12 R. I. Wu and J. H. Perepezko, Metall. Mat. Trans. A., 31A (2000) 497.
13 A. D. Cetel and D. N. Duhl, Superalloys 1988, The Metallurgical Society, Warrendale, PA 1988, p. 235.
14 P. Auburtin, PhD Thesis, University of British Columbia, Vancouver, BC 1998.