WALLCOLMONOY
HI TEMP BRAZING ALLOYS

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Melting Characteristics of Selected Brazing Filler Metals by Thermal Analysis; Differential Scanning Calorimetry (DSC)

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Abstract

In the early 1950's when nickel based brazing filler metals were being developed by Bob Peaslee at Wall Colmonoy, their solidus-liquidus temperatures were measured using thermal analysis during cooling. The plot of temperature versus time during solidification was analyzed to determine changes in cooling rate, these so called arrests indicated a phase change. Solidus-liquidus data was eventually incorporated into standards such as AWS A5.8 currently in table B. 2[1], ASME BPVC.II.C-2015 table B. 2[2], and BS EN ISO 17672:2016 table 11[3].

In the early 1990's Mr. Peaslee began investigations regarding comparison of solidus-liquidus determination results between the cooling curve and differential thermal analysis (DTA).No conclusions were made and the cooling curve method was used by Wall Colmonoy until acquisition of a modern thermal analyzer in 2014.

This paper makes an effort to demonstrate the nature of differences in the melting characteristics of nickel base brazing filler metals due to shifts in elemental composition within the allowed specification ranges for said composition and variation of solidus-liquidus values obtained by different methods of thermal analysis. Multi-element filler metals are common, so the focus herein is upon relatively simple binary and ternary systems.

Obtaining accurate solidus-liquidus temperatures is important to ensure that:

1. Brazing temperatures are sufficiently high so as to be above the liquidus.

2. Any diffusion hold in the brazing cycle will be below the solidus and solid state diffusion can occur without inducing erosion of the base metal being brazed.

Introduction

Various commercial documents, such as AWS A5.8 and BS EN ISO 17672 provide standards for brazing filler metals. Additionally, some proprietary specifications either refer to, or define requirements for melting characteristics of particular filler metals. The melting characteristics of solidus-liquidus temperatures are generally referred to as single, nominal values for the filler metal of a nominal elemental composition. The method(s) used to determine these values at the time of inception of the AWS A5.8 were not well defined nor were they referenced in the Analytical Methods Informative Annex of the specification. Even today the relevant industry specifications do not define the analysis methods to be used in determination of these thermal characteristics.

Tabulated values in AWS A5.8 table B.2 and BS EN ISO 17672:2016 table 11 indicate a range in which melting occurs for non-eutectic alloys by listing single, separate values for solidus-liquidus. Specifying a single value for either solidus or liquidus does not provide for the variation of these individual thermal characteristics due to variation in composition. For eutectic alloys a single value is given for the solidus and repeated for the liquidus. This specification scheme provides even less flexibility for the reasonable variation of eutectic alloy compositions and does not take into account the dynamics of various thermal analysis methods. Although the specifications do currently caveat tabulated melting temperatures as "approximate values", more precise language is needed in order to prevent misunderstanding and misuse of the specifications.

This paper offers a rudimentary examination of thermal analysis methods which can be used to determine solidus-liquidus temperatures and how they may relate to observed differences within the composition ranges for a few filler metal alloy systems.

Discussion

Before the availability of more modern standards for thermal analysis (ASTM E794[4] or PrEN 3877[5]) use of a simple "cooling curve" method was used to detect the temperatures at which phase changes occur in an alloy sample. The cooling curve method records the temperature versus time during cooling of a liquid metal as it transforms to a solid. During the actual solidification event, theoretically, the temperature of the sample will not change until the entire sample has released (exothermic reaction) a sufficient quantity of heat known as the latent heat of fusion so as to allow the entire sample to undergo the phase transition. The temperature versus time chart will generally indicate a falling temperature with a stabilization of the temperature for the duration of the phase transition, and then a resumed falling temperature after the solidification event has concluded. For example, Figure 1 shows the result of a single cooling curve test for Nicrobraz® 150 (BNi-9) filler metal, the flat portion of the curve indicates the solidification event.

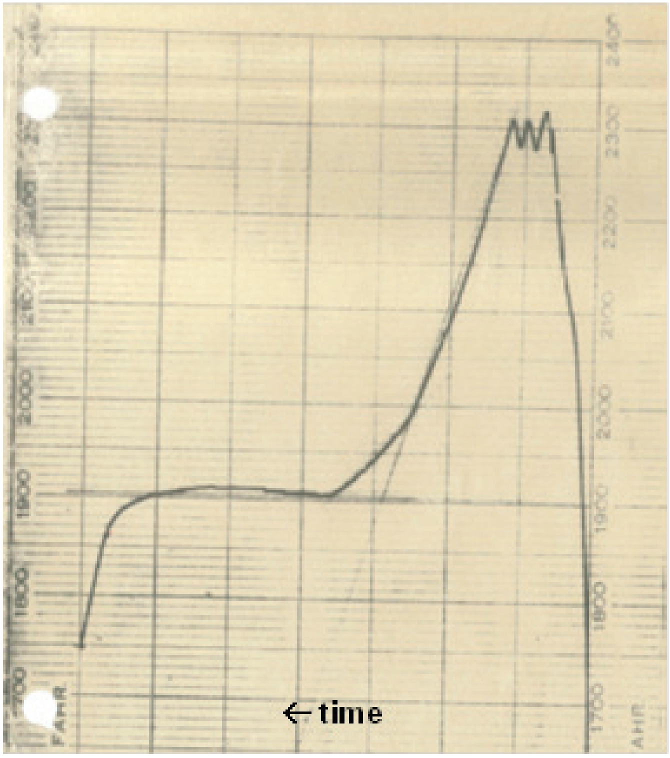

Figure 1. Cooling curve for Nicrobraz® 150 (BNi-9) conducted in April 1956 by Wall Colmonoy Corporation. Cooling rate ~6.5°C/min. Solidus ~1040°C; Liquidus ~1046°C[6]. Photocopy of a scrolling autopen chart recorder where time is increasing from right to left. The temperature spike at the right side indicates initial contact between thermocouple and liquid metal sample.

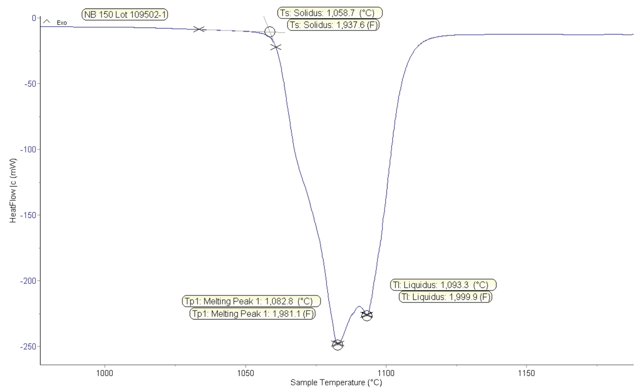

Figure 2. shows thermal analysis results, also for Nicrobraz® 150 (BNi-9) following EN 3877 method modified for Differential Scanning Calorimetry (DSC). Heating curve, (10°C/min), temperature versus heat flow, indicates solidus of 1058.7°C and liquidus of 1093.3°C.

Nicrobraz® 150 (BNi-9) is a ternary alloy with the composition: Ni-15Cr-3.6B which targets the ternary eutectic composition. Table 1 summarizes AWS information for this filler metal.

Standard	Boron	Chromium	Solidus °C	Liquidus °C
Nicrobraz® 150 (BNi-9)	3.25 - 4.00	13.5 - 16.5	1055	1055
Mid range	3.625	15		

Table 1

The main factor which comes into play during data recording for any method is resolution, in the case of thermal analysis this refers to how often the sample temperature can be recorded. If the resolution is insufficient then an event of a short duration will either not be recorded completely or may not be detected at all. Controlling the heating/cooling rate during a thermal analysis is one way of insuring a recording system's resolution is sufficient to capture all thermal events of interest. Using the legacy cooling curve method the cooling rate may be controlled if the sample is kept in the furnace during cooling or uncontrolled if the sample is removed from the furnace during the cooling. In Figure 1 it is unknown if the cooling rate is controlled or not. Although DSC and DTA are widely regarded as highly accurate, heating and cooling rates have a direct effect upon that accuracy, generally the lower the rate of temperature change, the more accurate the analysis will be. Neither of the curves in Figure 1 (cooling curve) or Figure 2 (DSC) indicates congruent melting compositions as features of both methods indicate multiple phase change events.

Table 2 has DSC data for 6 lots with boron content below and above the mid-point of the AWS range. This data indicates that none of the lots exhibit congruent melting with a maximum difference between solidus-liquidus temperatures of 23.5°C and an average difference of 20°C.

DSC	B	Cr	Solidus °C	Liquidus °C
Lot 1	3.41	14.4	1061.9	1078.6
Lot 2	3.47	15.1	1057.6	1081.1
Lot 3	3.49	14.8	1061.1	1079.3
Lot 4	3.96	14.2	1059.4	1080.4
Lot 5	3.9	15.1	1058.4	1079.6
Lot 6	3.84	14.9	1060.9	1080.3
Average	3.68	14.8	1059.9	1079.9
Std. Dev.	0.25	0.37	1.69	0.89

Table 2

The DSC results for solidus temperature in Table 2 differ from AWS A5.8 solidus temperature by 5°C on average.

Table 3 shows some additional legacy cooling curve data for Nicrobraz® 150 (BNi-9) which does not correlate with either the solidus or liquidus temperatures shown in AWS A5.8 or with the DSC results.

Cooling Curve	Solidus °C	Liquidus °C
Apr-56	1040	1046
Oct-93	1040	1046
Sep-92	1043	1068
Sep-92	1041	1046
Average	1041.0	1051.5
Std. Dev.	1.41	11.00

Table 3

Similarly, data was compiled for the Nickel-Phosphorous binary alloy filler metal Nicrobraz® 10 (BNi-6) which is targeted at the binary eutectic composition of Ni-11P. Table 4 shows the DSC data which correlates fairly closely with the solidus temperature called out in AWS A5.8 of 877°C.

DSC	Phosphorus	Solidus °C	Liquidus °C
Lot 1	11.08	884.6	910.4
Lot 2	11.59	884.6	909.7
Lot 3	11.33	885.4	912.6
Lot 4	10.16	884.3	906.9
Lot 5	10.34	884.4	906.6
Average	10.90	884.7	909.2
Std. Dev.	0.62	0.43	2.51

Table 4

Again it is seen that DSC yields results which illustrate non-congruent melting behavior through much of the allowable 10.0% to 12.0% range for phosphorus.

Table 5 shows results when thermal analysis by the cooling curve method is done for Nicrobraz® 10 (BNi-6). The Nickel-Phosphorous binary phase diagram7 shows the eutectic composition at 11% phosphorus with melting temperature of 880°C. The cooling curve data for phosphorous at 11.2% to 12.0% show liquidus temperatures scattered around 880°C with low solidus temperature results pointing to poor correlation between AWS A5.8 composition ranges and the associated solidus-liquidus values. In contrast the DSC data shows a solidus temperature across a wide range of phosphorous composition within the allowable range to be very consistent and only about 5°C above the expected solidus value.

Cooling Curve	Phosphorus	Solidus °C	Liquidus °C
64623-2	11.8	871	880
64623-1	11.9	867	882
64499-5	11.2	872	875
64385-1	12.0	849	877
Average	11.7	864.8	878.5
Std. Dev.	0.4	10.7	3.1

Table 5

The three DSC charts shown in figure 3 are for Nicrobraz® 10 (BNi-6). While each of the lots represented conform to the Nicrobraz® 10 (BNi-6) composition limits, the DSC charts clearly show that the melting characteristics are distinctly different exhibiting a single melting event as expected by a eutectic alloy in the first case, in the second case two distinct melting events are evident, and in the third case a more complex behavior is seen showing multiple melting events. Although the solidus temperatures are within a few degrees of one another and the liquidus values vary only slightly more (about 6°C), it is obvious that the samples exhibit incongruent melting compositions. This clearly demonstrates that even in a simple binary eutectic alloy; small variations in elemental composition within the specified ranges will depart from the eutectic composition and its expected thermal characteristics.

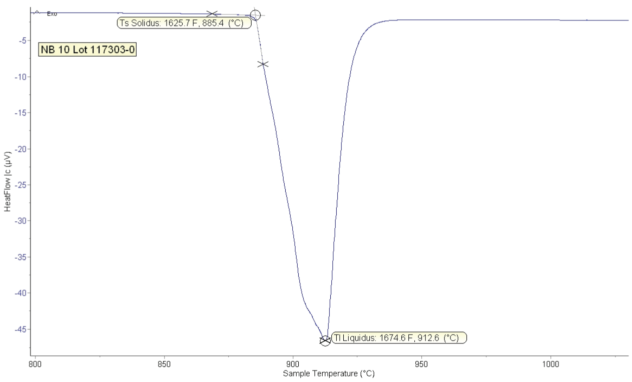

Figure 3a shows a DSC chart for Nicrobraz® 10 (BNi-6) with 11.33% Phosphorous and indicating slightly incongruent melting.

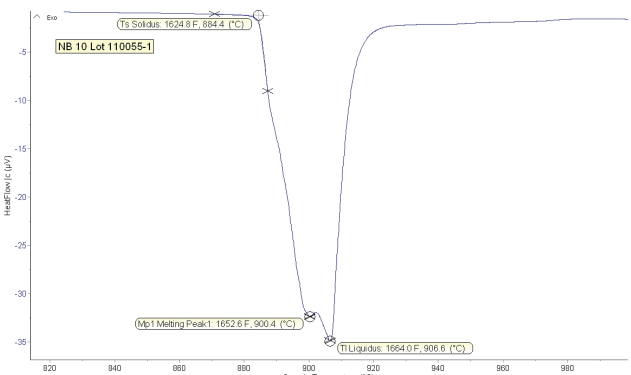

Figure 3b shows a DSC chart for Nicrobraz® 10 (BNi-6) with 10.34% Phosphorous and indicating incongruent melting.

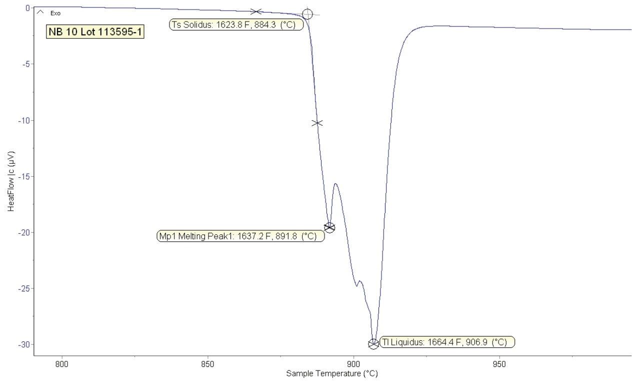

Figure 3c shows a DSC chart for Nicrobraz® 10 (BNi-6) with 10.16% Phosphorous and indicating incongruent melting.

Extensive cooling curve and DSC data have been compiled for a more complex quaternary system; Ni-29Cr-6P-4Si (Nicrobraz® 152 (BNi-15). Table 6 shows the data collected over time for 188 lots of powder. On an average basis the difference between cooling curve and DSC methods is 30°C for solidus and 17°C for liquidus. This degree of difference illustrates the potential importance of specifying the determination method for melting characteristics to avoid problems in selection of brazing furnace cycles.

Method	Cooling Curve	DSC
Avg. Solidus(°C)	955	985
+/- 3 Sigma Solidus	929-980	964-1005
Avg. Liquidus (°C)	1026	1009
+/- 3 Sigma liquidus	970-1082	990-1028
Data Sets	53	135

Table 6

Table 7 shows the average composition for the data sets summarized in Table 6.

Element	Cooling Curve	DSC
Cr	29.0	29.7
P	5.9	6.1
Si	4.2	4.0

Table 7

Summary

The history of the AWS A5.8 specification dates back to 1952 when *AWS A5.8-52T Tentative Specification for Brazing Filler Metal* was published based on *Proposed Tentative Specifications for Brazing Filler Metals*[8,9] in volume 31, the August edition of The Welding Journal. Although the terms solidus and liquidus are defined and simply explained within the scope of the tentative specification; the method(s) used in the determination of their values for each alloy are not disclosed or explained. Additionally, the document points out the difference between solidus-liquidus and Melting Point/Flow Point and cites the definite nature of the former and the ambiguous nature of the later as the cause for the use of Solidus-liquidus values in the tentative specification. In that first issuance of the tentative specification, the solidus-liquidus values presented were not explicitly assigned to the nominal composition for each alloy; however, in later revisions of A5.8 the Solidus-liquidus tables in the specification were updated with a footnote indicating that the values given for solidus-liquidus are for the nominal composition of each alloy. Other industry standards such as BS EN ISO 17672:2016 also refer to solidus-liquidus temperatures as approximate values. Appropriately; this implies that the solidus-liquidus values vary with composition even within the relatively narrow specification limits of the alloy's composition. Furthermore; Eutectic compositions are regarded highly as brazing fillers because they help save time and money during brazing cycles by minimizing brazing temperatures, also these eutectic compositions help to minimize issues such as liquation because of the single melting point of a eutectic composition. Specifications for alloys which target eutectic compositions have composition ranges for the constituent elements within reasonable limits for mainstream production methods; however, even slight variations from the eutectic composition will produce melting behaviors which are not characteristic of eutectic compositions.

The normal usage of brazing filler metals in Aerospace, Automotive, and other Industrial/Commercial applications represent significant economic investment and cash flow in our society. With an economic impact certainly worth many millions of US dollars; the brazing process, its first pass yields and process improvements are very important. In order to provide brazing businesses with means for their engineers to control and predict the outcomes of their operations technical data such as melting characteristics are important.

One option to have a better understanding between specified composition ranges and their associated solidus-liquidus temperatures would be to consider a scheme for the solidus-liquidus temperature table in which upper and lower limits are provided for all specified alloys including those which target eutectic composition rather than providing only the values for the nominal composition with the footnote to that effect. A second option is for brazing engineers to obtain solidus and liquidus data for the filler metals in use and develop process improvements based on this information in conjunction with their process data.

The Analytical Methods Annex of AWS 5.8 and respective sections of other industry standards should be updated to include modern thermal analysis methods approved for use in the characterization of brazing filler metals. Given the number of publications relating to this topic (such as NIST Special Publication 960-15[10]) the method should include details regarding (for example) first melting vs. second melting, heating/cooling rate, holding temperatures, the definition of individual thermal characteristics (i.e. event magnitude, alloy homogenization, etc), as well as the method of instrument calibration.

References

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