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Microcalorimetry on Metastable Beta Phase Alloys Subjected to Applied Stress

C.J. Elvidge and C.M. Friend

Dept. of Materials Science and Engineering Cranfield University, Shrivenham Campus, Swindon, England

Abstract: The development of a High Sensitivity Scanning Stress Microcalorimeter for the study of martensitic phase transformations in beta phase CuAlNi single crystal tensile specimens is described. The design of this system is discussed with reference to an earlier version. The values of calorimetric sensitivity reported for the new system represent a significant improvement over the prototype and a comparison is made. More significantly, the new sensitivity values compare directly with those reported for stress free instruments employing similar detectors indicating that many of the problems associated with calorimetric measurements under stress have been considerably reduced.

1. INTRODUCTION

The thermodynamic behaviour associated with stress induced thermoelastic martensitic phase transformations in noble metal β phase alloys has been the focus of much recent research [1,2]. Determination of entropy and enthalpy changes which occur are essential for an understanding of the complex stress/temperature phase equilibria present in these alloy systems. An established experimental technique for such thermodynamic investigations is to isothermally test tensile specimens of the chosen alloy system at different temperatures to obtain the Stress / Temperature Phase Diagram. This is then followed by calculation of the entropy changes using the Clausius-Clapeyron equation. The enthalpy change can then be deduced from the assumed stress independent entropy value and an estimated value of the equilibrium temperature between the phases at zero stress.

A complimentary technique for the determination of these fundamental thermodynamic criteria would be to use a calorimetric route. Historically this has evolved from the use of solid state detectors on unstressed samples [3,4]. The detectors, often Bismuth Telluride thermobattery modules, have an operating range of 100 to 380K and display a high sensitivity when connected in differential. The behaviour of these differential scanning calorimeters in the study of phase transformations occurring in shape memory alloys has been described in detail elsewhere [5]. When using modifications of the above techniques to investigate the effect of stress on the system two approaches are available, either stress inducing the transformations at constant temperature or thermally inducing them at constant stress. Sade et al [6] used the former approach to demonstrate the feasibility of using a solid state calorimetric detector on a CuZnAl single crystal whilst concurrently recording the pseudoelastic stress strain curve produced. However, the relatively low level of thermal sensitivity reported for the detector used ($< 50 \text{ mVW}^{-1}$) led to only qualitative conclusions. A similar detector has been more successfully employed to study thermally induced transformations at constant stress [7]. Friend et al, in a technique described in detail in [8] produced a prototype stress calorimeter of sufficient sensitivity (170 mVW^{-1}) to enable direct measurement of enthalpy and entropy changes in a transforming single crystal CuAlNi alloy sample. Good agreement was found between these results and those produced by isothermal stress induced transformation.

The aim of this paper is to report the development of a scanning stress calorimeter of enhanced sensitivity based upon the design of this prototype.

2. SYSTEM DEVELOPMENT

Considerable experimentation revealed design problems with the prototype which could be improved upon. Most importantly, it was found that thermal losses from the specimen through the grips led to a reduction in expected sensitivity. Values of $\sim 300 \text{ mVW}^{-1}$ have been regularly reported for stress free instruments employing similar detectors [9]. Careful selection of materials used in the construction of the grip faces would reduce these thermal losses. Significant drift in the calorimetric signal was also experienced. Its stability seemed to be dependant upon a loss of differentiability during measurement coupled with a relatively low level of thermal buffering employed in the heating/cooling chamber. A redesign of the central core utilising a more substantial calorimetric block would appear theoretically to both thermally buffer the detectors and allow equilibrium heating and cooling to reduce spurious differentiability. Because of the fragile nature of the detectors, and the need to change load and/or samples it was discussed that any redesign should ergonomically facilitate this. A primary requirement with this in mind, was the construction of an independent frame in which to house the instrument and weight carriage, as the prototype relied on building structure for support.

2.1 The Experimental System

The central core of the calorimeter consisted of two Bismuth Telluride semiconductor thermobattery modules (Melcor FC 0.24-66-05 [10]) connected in differential and mounted inside a substantial cylindrical two-piece brass calorimetric block. This is shown in Fig. 1.

Fig 1 The Calorimeter Central Core Assembly

The 'hot' face of one thermobattery was in direct thermal contact with one face of the tensile specimen whilst the 'hot' face of the other was in contact with the reference sample. The 'cold' face of both batteries were in direct thermal contact with, and separated by, a ligament of the calorimetric block. A layer of 1mm thick polytetrafluoroethylene sheet insulated the block from the 'free' face of each specimen. The temperature was determined by a centrally embedded Pt 100 resistance connected to a digital thermometer. The core was self-gripping and small changes in specimen shape during transformation were accommodated by the action of a spring loaded clamping screw.

The core was surrounded by an AlMg heating/cooling jacket of hinged clamshell design and whose internal contours closely mirrored those of the Brass core. The jacket contained six cartridge type electrical heaters

and adjacent to these an internal reservoir acted as a vessel for liquid Nitrogen coolant pumped in from a separate dewar. Finally a self-foaming polyurethane resin cover was shaped to enclose the whole central assembly to ensure maximum insulation. Fig. 2. shows the calorimeter assembly and grips. The grips were of modified Instron type except the faces had been fitted with thermally insulating Zirconia double knife edges.

Fig 2 The Calorimeter Assembly and Grips

1. Grips	5. Calorimetric Block
2. Zirconia Knifedges	6. Cartridge Heaters (6 off)
3. Testpiece	7. Thermobatteries
4. Heating/Cooling Jacket	8. Thermocouple

A free standing frame of Rigid Steel Joist construction welded to a substantial steel baseplate was connected to the upper grip via a universal joint and 10^4 N load cell. Load application and positioning was achieved by means of an hydraulic jack. Excessive lateral movement of the load stack was prevented by adjustable steel support collars attached to the frame. Fig. 3. shows the calorimeter and weight carriage assembled in the frame. The calorimetric signal, output from the digital thermometer and load cell were recorded at predetermined intervals with an HP3457A digital multimeter via an internal multiplexer board. This was in turn, interfaced with a Thurlby-Thandar programmable power supply and an IBM compatible PC by its IEEE 488 bus. Operation of the system was from the computer console using software developed from National Instruments LabView for Windows. This enabled programs specifically designed to control the above individual instruments to be integrated into a single 'Virtual Instrument', the Scanning Stress Calorimeter. The software also stored the data in a format consistent with most available spreadsheet/graphics packages for subsequent analysis and presentation.

Fig. 3. The Calorimeter Weight Carriage and Frame Assembly

1. Load Cell	5. Lead Weights
2. Grips	6. Support Collars
3. Heating/Cooling Jacket	7. Hydraulic Jack
4. Adjustable Support Plate	

2.2 Calibration

A measure of the calorimetric sensitivity of the apparatus, as a function of temperature was required over the full range of operation (150-350K). This was achieved in a similar way to [7] by dissipating a known thermal power from a heating resistance testpiece designed to closely mimic the evolution of heat from an actual specimen undergoing transformation. The results of the calibration are displayed in Fig. 4, where a comparison is made with those of Ortin et al [8] over the same temperature range.

The experimental data produced may be fitted by the following parabolic equation:

$$S \text{ (mVW}^{-1}\text{)} = -0.002T(K)^2 + 1.8251T(K) - 67.933$$

and the curve is drawn through the experimental data in Fig. 4. A large scatter of data is observed, notably at lower temperatures. This is due to an insufficient number of tests to produce a significant statistical treatment. These results indicate an at least 70% improvement in sensitivity across the full range of operation when compared with the prototype. However, if the same calibration procedure was attempted on the central core with no grips attached, consistent sensitivity values in excess of 400mVW^{-1} at room temperature were recorded. This would seem to indicate that there still exists a potential 25% improvement in sensitivity which may be obtained by further experimentation with grip design.

2.3 The Heating/Cooling Cycle

The differential nature of the detector arrangement necessitates low scanning rates $<0.5\text{K}\cdot\text{min}^{-1}$ to allow maximum resolution of the transformation signal from the calorimetric baseline. On the heating cycle a near ideal heating rate was established without external control until ambient temperatures were achieved. Then 240V cartridge heaters incrementally ramped from 0-100V max. provided the means to reach $\sim 330\text{K}$ without unduly affecting the calorimetric signal. Cooling the system from ambient temperatures was more problematic. The liquid Nitrogen coolant pumped into the cooling jacket reservoir without careful flowrate control produced significant calorimetric baseline drift caused by non equilibrium conditions in the central core making any transformation signal interpretation a difficult task. This was relieved somewhat by the improved signal to baseline ratio produced by this system. Example heating and cooling rate curves are displayed in Figs. 5 and 6 with their respective calorimetric baselines. Further work is necessary to improve the cooling cycle. This will probably take the form of increased thermal buffering of the Nitrogen reservoir.

Fig 4 Calorimetric Sensitivity as a Function of Temperature

(♦) denotes experimental data values for the current instrument with Parabolic fit

(■) are parabolic fit values for the prototype instrument [8]

Fig 5 and 6 The Heating and Cooling Cycle

(TB pd is the Thermobattery output in mV.)

3. SUMMARY

A self contained high sensitivity scanning stress calorimeter has been produced. Its operation is that of an independent instrument controlled directly from the computer console.

The values of calorimetric sensitivity obtained at room temperature (300mVW^{-1}) represent an $\sim 80\%$ improvement over the prototype upon which the design was based. More significantly these values compare directly with those reported for stress free instruments employing similar detectors, indicating that many of the problems associated with measurements under stress have been considerably reduced.

This instrument is currently employed in the investigation of martensitic transformations occurring in a family of single crystal CuAlNi alloys previously reported upon [8]. This is both to complete its commissioning, and to demonstrate its performance and applicability for the thermodynamic mapping of other shape memory systems.

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