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Decontamination in the EPMA with a Peltier-cooled cold finger

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Abstract

A prototype Peltier thermoelectric cooling unit has been constructed to cool a cold finger on an electron microprobe. The Peltier unit was tested at 15W and 96W, achieving cold finger temperatures of -10°C and -27°C respectively. The Peltier unit did not adversely affect the analytical stability of the instrument. Heat conduction between the Peltier unit mounted outside the vacuum and the cold finger was found to be very efficient. Under Peltier-cooling, the vacuum improvement associated with water-vapour deposition is not achieved; this has the advantage of avoiding the severe degradation of the vacuum observed when warming up a cold finger from liquid nitrogen temperatures. Carbon contamination rates reduce as cooling commences; by -27°C contamination rates were found to be comparable to liquid nitrogen cooled devices. Peltier cooling therefore provides a viable alternative to liquid nitrogen-cooled cold fingers, with few of their associated disadvantages.

Introduction

Liquid nitrogen (LN_2) cold fingers have been routinely used in electron probe microanalysis (EPMA) for many years to reduce carbon contamination and thereby aid the analysis of light elements (Bastin & Heijligers 1986, 1988, 2011). A key application driving developments in anticontamination for EPMA was and remains the analysis of low concentration carbon in ferrous alloys (Ong 1966, Swaroop 1973 and Yamashita et al. 2016).

Quantification at low accelerating potentials using field-emission gun EPMA (FEG-EPMA) to provide high spatial resolution, has become an important new area where contamination poses a significant problem (Merlet & Llovet 2012; Buse & Kearns 2015).At such low voltage or low over-voltage conditions, surface contamination build-up results in a significant reduction in the landing energy of the beam, as well as contributing to additional absorption of emitting X-rays (Reed 1975). The growth of low-voltage FEG-EPMA creates an impetus for developing a convenient and continuous anti-contamination device.

Previous studies have suggested that cooling a cold finger to the temperature of liquid nitrogen was not required for effective decontamination. Indeed, temperatures in the range of -15 °C to -70 °C are found to be effective for cold fingers of different geometries and distances from the sample (Komoda & Morito 1960; Borile & Garulli 1978; Ranzetta & Scott 1966; Ennos 1954; Hirsch et al. 1994). A detailed study by Hirsch et al. (1994) used a cold finger with the geometry of a cage surrounding, but not in contact, with the sample and cooled by LN_2 to varying temperatures. They demonstrated that temperatures of -25 °C were comparable to –135 °C in reducing contamination.

The implication that the temperature required can be significantly higher than LN_2 presents the opportunity for using a Peltier thermoelectric cooling unit. Peltier devices readily achieve -25°C (50°C below ambient) and more powerful or stacked devices can achieve greater degrees of cooling, approaching 80 – 90°C from ambient (e.g. Hsu et al. 1996). The principal advantage of Peltier cooling is the ability to run the cold finger over long periods of time, not limited by the size of a nitrogen dewar and the requirement to keep it filled. The absence of liquid nitrogen and the ability to run continuously would allow for the routine use of a cold finger for low voltage and light element

analysis. Laboratory managers will breathe a collective sigh of relief that the burden of keeping a cryogenic liquid in their domain has passed.

In this proof-of-concept study we have constructed a prototype Peltier-cooled cold finger. Using this prototype we have checked instrument analytical stability and assessed its effectiveness in anti-contamination.

Materials and Methods

A Peltier-cooled cold finger was constructed by modifying a JEOL LN_2 cold finger on a JEOL JXA8530F. The LN_2 flask was removed and replaced with a water-cooled Peltier system as shown in figure 1. The Peltier unit is mounted outside the vacuum and consists of two Peltier devices (TEC1-12706) on either side of a central aluminium block. This central block is cooled and attached to the existing copper rod and cold finger of the JEOL cold finger assembly (see figure 1a-c), with each Peltier device possessing a water-cooled heat sink. To remove electrical interference on the electron beam the central aluminium block and the heat sinks were connected to earth.

The temperature of the cold finger was measured using a k-type thermocouple attached to the cold finger inside the chamber (figure 1d). For greater sensitivity the vacuum was measured using the millivolt read-out from the JEOL Penning gauge calibrated to the digital output.

Analyses were conducted on a carbon-coated polished andradite sample at 5 kV, 10 nA with a 1 µm beam size and a 10 µm spacing between analyses. Carbon-coated andradite was chosen as carbon is commonly used as a coating material in the analysis of silicate materials, developing on the work of Buse & Kearns (2015) examining methods of mitigating contamination in high-resolution low-voltage silicate analysis. After inserting samples into the analysis chamber, the instrument was left pumping for 2-3 hours to recover vacuum prior to cooling the cold finger. The initial vacuum at the start of the cooling experiments was comparable for both the Peltier test (3.6-3.7 x 10^{-4} Pa) and the LN_2 test (3.6 x 10^{-4} Pa).

Calibrated backscattered electron (BSE) images were used to measure the amount of contamination build-up adjacent to the beam, similar to the method described by Buse & Kearns (2015). The BSE image intensity was calibrated for carbon thickness using two andradite samples with carbon coat thicknesses of 25 nm (the irradiated sample) and 32 nm respectively (measured in Buse & Kearns 2015, using the thin film package GMRFilm). The contamination was measured by extracting line profiles through analysis spots from the calibrated images. For each contamination measurement the average of 3-4 analysis points was used.

Results

Beam stability, temperature and vacuum

The Peltier unit does not degrade beam stability - the probe current remained stable whilst the Peltier unit was operating (Figure 2a) and beam shift when turning the Peltier unit on was 20 nm (Figure 2b). Table 1 gives the minimum temperature of the cold finger using LN_2 and Peltier cooling. The Peltier unit was tested at two different power settings (15W and 96W). The heat conduction is efficient; the Peltier unit outside the vacuum recorded a temperature of -29°C when the cold finger inside the chamber recorded a temperature of -27°C. There is uncertainty in the minimum temperature of the cold finger achieved when using LN_2, because K-type thermocouples are insensitive in this range. The measured temperatures of -171°C and -215°C using a Eurotherm gauge and the Omega thermocouple reference tables respectively reflect this and the actual temperature given the efficient heat conduction of the cold finger must be close to and not exceed -196°C the boiling temperature of LN_2.

Figure 3a compares the time scale required for cooling the cold finger using LN_2 and Peltier cooling. Increasing the power supplied to the Peltier unit results in a more rapid initial cooling and a lower minimum temperature. Similarly with LN_2 initial cooling is more rapid and the minimum temperature is much lower than the Peltier unit. The effect of temperature on vacuum pressure is given in Figure 3b. Over the temperature range of Peltier cooling the vacuum pressure remains approximately constant. Conversely, over the temperature range of LN_2 cooling, a step-change is observed in the vacuum level at ca. 115°C as the vapour pressure of water is crossed (-111°C at 1.33×10^{-4} Pa; Honig & Hook 1960). This change in vacuum explains why we observe the severe degradation of the vacuum on warming up the cold finger after LN_2 cooling, which is not observed with Peltier cooling.

Contamination rates

During spot analysis carbon contamination forms ring shape deposits as hydrocarbons cracked by the electron beam deposit adjacent to the beam position (e.g. Castaing & Descamps 1954; Ranzetta & Scott 1964; Fourie 1976). In this study, contamination is quantified using BSE images calibrated for carbon thickness. The amount of contamination was measured at different temperatures by running a series of spot analyses (each for 180 seconds) during both Peltier and LN_2 cooling of the cold finger. Contamination reduces as the cold finger is cooled. Figure 4 is a series of carbon Kα x-ray maps of spot analyses taken at different cold finger temperatures when cooled by the Peltier unit and the effect can be clearly seen. By measuring the amount of contamination using calibrated BSE images, contamination is observed to reduce to similar levels for both LN_2 and Peltier cooling (Figure 5). The temperature at which minimal amounts of contamination is achieved is -27 °C for Peltier and -75°C for LN_2 cooling.

Line profiles of the carbon contamination associated with spot analyses are given in Figure 6a. The profiles show the build-up of carbon with time. The data plotted is for cold finger at room temperature, -27°C using Peltier cooling and -196°C using LN_2 cooling. Contamination thickness proceeds in a very similar manner for Peltier and LN_2 cooling (Figure 6b). Consistent with previous studies (e.g. Hirsch et al. 1994, Bastin & Heijligers 1988, 2011), when using a cold finger (Peltier or LN_2 cooled) there is initial deposition during the first minute which quickly drops off, whereas for the case without anticontamination the rates are much higher and deposition continues with beam exposure time.

Discussion

Contamination is reduced to a similar amount with Peltier and LN_2 cooling. The discrepancy in the temperature at which this is achieved observed at -75°C for LN_2 and -27°C for Peltier cooling is consistent with a time lag response. The initial temperature drop using LN_2 is rapid, with the cold finger quickly passing from 20°C to – 50°C (see Figure 3a) preventing contaminate precipitation keeping pace with temperature change. Given this, -27°C is a more accurate estimate of the minimum temperature required for effective anticontamination, which is consistent with the previous work by Hirsch et al. (1994) and comparable to that of Heide (1963), where the minimum contamination was reached at about -40°C. The reason for an absence of further improvement when cooling the cold finger to liquid nitrogen temperatures is unclear. Heide & Urban (1972) record the temperature at which hydrocarbons start to condense as 6.8 °C with the partial pressure of hydrocarbons approaching 1 nTorr at -93.16 °C. The critical temperature will depend on the species of hydrocarbons present, with the vapour pressure of mechanical oil crossed at ca. -10°C, whilst vacuum grease (apiezion L) is always below vapour pressure. Surfaces of the chamber on venting and of samples inserted into the machine also absorb a range of hydrocarbons with Campell & Gibbons (1966) ascribing the gradual reduction in hydrocarbon contamination to the crossing of a

series of vapour pressures, and Hart et al. (1970) recording the presence of alkanes and alkenes which condense at temperatures <-75°C.

It is unclear whether the carbon coat has an effect on the contamination rate or the temperature at which minimum contamination is observed. However, the data shows a close agreement with that of Hirsch et al. (1994) for uncoated polished copper.

Restricting the cold finger to temperatures above the vapour pressure of water has a big advantage in avoiding the severe degradation of the vacuum when warming up the cold finger. It also greatly reduces the amount of contaminants deposited on the cold finger, water being the main gas species in the chamber (Hart et al. 1970; Heide & Urban 1972). The use of a Peltier unit allows long-term operation without the need for LN_2 refilling. The long-term performance is unknown; as the cold finger becomes progressively coated in contaminants its performance may deteriorate, requiring periodic warming-up, similar to cryogenic pumps (Ash 1998). This effect will be greatly reduced compared to cryogenic pumps by not depositing water vapour on the cold finger, lengthening the time of operation.

The data suggests that cooling beyond -27°C is not required. The absolute temperature achieved by the Peltier is dependent on the room temperature (kept constant at 21°C in this study) and the temperature of the water used to cool the heat sinks. Initial tests were run with cold mains water. Warmer water will reduce the temperature difference between the hot and cold sides of the Peltier devices and reduce the amount of cooling achieved. To ensure -27°C is always achieved more powerful Peltier devices or an increased number of devices is suggested for a revised Peltier unit. A closed-circuit chilled water supply would also be beneficial.

The results suggest that there is no need to mount the Peltier unit within the vacuum chamber as the heat transfer between the Peltier unit and the cold finger is effective. In addition a Peltier unit within the vacuum chamber may have adverse effects on the electron beam as some form of heat extraction would be required. A disadvantage of mounting the Peltier unit outside the vacuum is that ice build-up was found to occur around the central cooled block over several days of operation. Improved insulation is required for a revised Peltier unit, excluding air from the cold surfaces.

Conclusions and future refinements

The anti-contamination performance of the prototype Peltier cooled cold finger when cooled to -27°C is similar to a liquid nitrogen cooled cold finger. This is consistent with the results of Hirsch et al. (1994). The Peltier unit was mounted outside the vacuum. It produced efficient cooling of the cold finger and did not degrade the performance of the instrument. Peltier cooled cold fingers are thus demonstrated viable and will provide a good alternative to LN_2 cooling. They have the potential to run for extended periods of time, although periodic conditioning of the cold finger may be required.

Two issues identified with the current prototype are: (1) ice deposition on the central cooled block mounted outside the vacuum and (2) maintaining the required temperature of -27°C to minimise contamination. To avoid ice deposition some form of air-tight insulation is recommended, probably through employing improved insulators. To ensure -27°C is always achievable the use of additional or more powerful Peltier devices requires to be tested; at present we only achieve -27°C operating the devices at their maximum power capacity. A chilled water supply to the heat sinks will further enhance heat transfer.

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