Thermal Analysis of Cobalt Chloride using DSC

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Abstract: ***My topic of thesis is Thermal Analysis of Cobalt Chloride using Differential Scanning Calorimetry. My aim is to improve the properties of cobalt and to increase its efficiency. Also the plant in which my thesis work is going check where Cobalt chloride can use or not behalf of any other automobile metal. Differential Scanning Calorimetry Shows that how can we improve hardness, Thermal Conductivity, Melting Point, boiling Point, We will Compare Ni(Nickel) with CO (Cobalt). We are trying To measure Error and calculate proper Result or Analysis that what are differences between Aluminium & Cobalt and we can use at which point to increase Efficiency. Differential Scanning Calorimetry already uses many other areas to Differentiate Metal's Thermal Analysis.***

Keywords: DSC

1. Introduction

1.1 Cobalt Chloride

Cobalt (II) chloride is an inorganic compound of cobalt and chlorine, with the formula $CoCl_2$. It is usually supplied as the hexahydrate $CoCl_2 \cdot 6H_2O$, which is one of the most commonly used cobalt compounds in the lab. [1]

The dihydrate is purple and hexahydrate is pink[1], whereas the anhydrous form is sky blue. Because of the ease of the hydration/dehydration reaction, and the resulting color change, cobalt chloride is used as an indicator for water in desiccants.
Niche uses of cobalt chloride include its role in organic synthesis and electroplating objects with cobalt metal.

Cobalt chloride has been classified as a substance of very high concern by the European Chemicals Agency as it is a suspected carcinogen.

1.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry, or **DSC**, is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

The technique was developed by E. S. Watson and M. J. O'Neill in 1962,[1] and introduced commercially at the 1963 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. The first adiabatic differential scanning calorimeter that could be used in biochemistry was developed by P. L. Privalov and D. R. Monaselidze in 1964 at Institute of Physics in Tbilisi, Georgia.[2] The term DSC was coined to describe this instrument, which measures energy directly and allows precise measurements of heat capacity.[3]

1.2.1 Types of DSC:

- Power-compensated DSC, keeps power supply constant
- Heat-flux DSC, keeps heat flux constant

Description of DSC:
There are two types of DSC commercially available: Heat Flux (HF) Type and Power Compensation (PC) Type. Figure 22.01 shows the block diagram of HF and PC types.

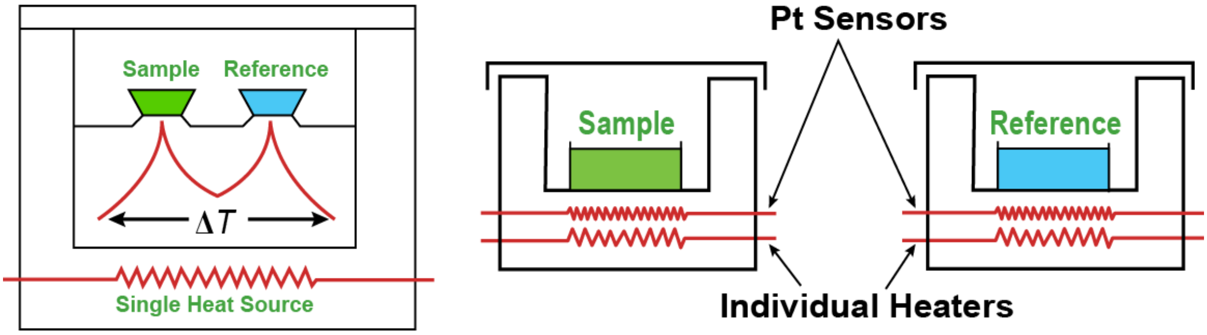


Figure 1.1: Schematic diagram of HF and PC types DSC

<u>In HF type DSC</u>
Both sample and reference pans are heated by a single furnace through heat sink and heat resistor. Heat flow is proportional to the heat difference of heat sink and holders. The temperature versus time profile through a phase transition in a heat flux instrument is not linear. At a phase transition, there is a large change in the heat capacity of the sample, which leads to a difference in temperatures between the sample and reference pan. A set of mathematical equations convert the signal into heat flow information. By calibrating the standard material, the unknown sample quantitative measurement is achievable.

In PC type DSC

Both sample and reference pans are heated by a different furnaces. When an event occurs in the sample, sensitive Platinum Resistance Thermometer (PRT) detects the changes in the sample, and power (energy) is applied to or removed from the sample furnace to compensate for the change in heat flow to or from the sample. As a result, the system is maintained at a “thermal null” state at all times. The amount of power required to maintain system equilibrium is directly proportional to the energy changes occurring in the sample. No complex heat flux equations are necessary with a power compensation DSC because the system directly measures energy flow to and from the sample.

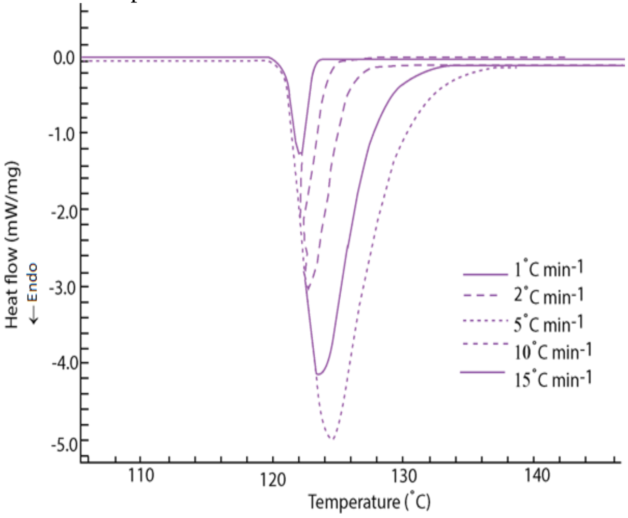
In addition, PC type DSC has enhanced modulated temperature DSC (StepScan) technique and fast scan DSC (Hyper DSC) for dramatic improvements in productivity, as well as greater sensitivity. Furthermore, the heating and cooling rate of PC types DSC can be as high as 500°C/min.

1.3 DSC Curves

The result of a DSC experiment is a curve of heat flux versus temperature or versus time. There are two different conventions: exothermic reactions in the sample shown with a positive or negative peak, depending on the kind of technology used in the experiment. This curve can be used to calculate enthalpies of transitions. This is done by integrating the peak corresponding to a given transition. It can be shown that the enthalpy of transition can be expressed using the following equation:

$$H = KA$$

where **H** is the enthalpy of transition, **K** is the calorimetric constant, and **A** is the area under the curve. The calorimetric constant will vary from instrument to instrument, and can be determined by analyzing a well-characterized sample with known enthalpies of transition



1.2 Analysis of Heat flow vs Temperature

2. Application

- DSC analysis is used to measure melting temperature, heat of fusion, latent heat of melting, reaction energy and temperature, glass transition temperature, crystalline phase transition temperature and energy, precipitation energy and temperature, denaturization temperatures, oxidation induction times, and specific heat or heat capacity.
- DSC analysis measures the amount of energy absorbed or released by a sample when it is heated or cooled, providing quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes.
- Only non-corrosive samples can be analyzed in this very sensitive instrument. No organic or other materials containing F, Cl, Br, or I may be submitted for DSC analysis without our knowledge. The customer must either tell us what the material is or at least that it is non-corrosive to metals and assume responsibility for possible replacement of a $3000 DSC cell if a cell is destroyed as a result of the analysis of their sample. Or, you may have us perform such analysis as may be needed to determine what the material is and whether it can be analyzed in the DSC. Sometimes a higher temperature DSC to which we have access may be able to handle somewhat more corrosive samples in the lower temperature range.

2.1 DTA (Differential Thermal Analysis)

With DTA/DSC, various types of information are sought such as the temperatures for phase transformations in alloys. The most common measurement involves determination of liquid us and solidus temperatures. These terms will be used to refer to thermodynamic quantities that depend only on the alloy composition (at fixed pressure). For phase diagram research, one might also want to determine other thermodynamic temperatures associated with melting and freezing; e.g., in binary alloys, invariant reaction temperatures and their character; viz., eutectic and peritectic. In ternary and higher order systems, information is sought regarding additional thermodynamic transitions with one or more degrees of freedom. Related measurements of interest can include the amount of super cooling possible prior to solidification and the micro structurally and solid diffusion rate-sensitive final freezing temperature/incipient melting point. One might want to know the super cooling tendency of a particular alloy in contact with a certain type of crucible or in the presence of a grain refiner. These temperatures are not purely thermodynamic in origin, but are needed for the modeling of castings, for the determination of maximum heat treatment temperature, etc. The DTA/DSC may at times be used for the identification of alloys from within a small class of alloys as a quality control method; i.e., the DTA plot could be used as a “finger print” of the alloy.

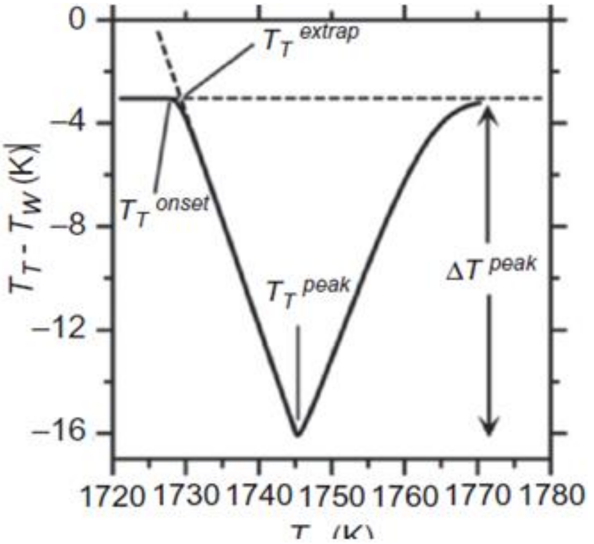
2.2 Initial Metallurgical State of Alloy Samples

At heating rates typical of a DTA, one cannot be certain that the microstructure of an alloy sample is in global equilibrium prior to or during analysis. A characteristic time required to eliminate spatial concentration gradients within phases is l2/4DS where DS is the solid diffusion coefficient and l is a distance that characterizes the modulation of the concentration. Near the solidus, DS is typically 10 _13 m^2/s for substitutional solutes or 10-10 m^2/s for interstitial solutes. For samples cooled at rates between 5 and 15K/min, the typical spacing of dendritic solidification structures is approximately 100–200mm. Hence, hold times of the order of 105 or 102 s may be required for the homogenization of substitutional or interstitial alloys, respectively. For interstitial alloys, normal thermal equilibration of the instrument prior to scans is usually sufficient to eliminate concerns about the prior homogeneity state of the sample and global equilibrium is likely to be maintained at slow scan rates in the DTA. However, the micro structural state of the substitutional materials must always be considered. If the user wants to determine the thermodynamic solidus, a series of melting runs following isothermal holds at successively higher temperatures below the proposed solidus value should be conducted to ensure that the sample has been annealed into an equilibrium structure.

2.3 Temperature Calibration: Choice of Onset Temperature

In normal DTA where the thermocouple is not immersed directly into the sample, the thermal lags cause the linear portion of the peak shape as well as a less sharp demarcation of the initiation of melting. This loss of sharpness can lead to difficulties of calibration for highly precise work. In Fig 4.1 the temperature of the first detectable·

Deviation from baseline is labeled $T^{Tonset.}$



4.1 T(K) Vs $T_T – T_W$(K)

The subscript T is used to denote thermocouple temperatures. Due to the inherent trouble of picking this temperature experimentally and due to the noise in the data, an alternative melting onset temperature is commonly employed. This procedure takes advantage of the fact that the thermocouple temperature versus time, TT(t), curve quickly becomes linear after the melting onset; the onset temperature, T_T^{extrap} is taken as the intersection of a linear fit to the downward sloping linear section of the melting peak and the extrapolation of the baseline. Both T_T^{onset} and T_T^{extrap} deviate from TM by an amount that depends on the heating rate and on the sample mass through the parameter r and the time constants, which depend on the area of contact between the sample and the cup see Fig 4.1 Thus, calibration should ideally be conducted for a mass and heating rate similar to those that will be used for the test samples.

$$T_T^{onset} = T_m + a\,(t_{s,cp} – t_{T,c})$$

$$T_T^{Extrap} = T_m + a\,[t_{s,c}\,(t_{s,cp} + t_{w,cp} + t_{w,,c})/(\,t_{s,c} + t_{w,,c})]$$

where $t_{s,c}$, $t_{T,c}$, and $t_{w,,c}$ are time constants characteristic for heat transfer in the instrument, a is the heating rate, TM the melting temperature, and r is the density. It can be shown that picking the first sign of melting actually has a smaller deviation from the true melting point and smaller heating rate dependence than the onset determined by the extrapolation procedure. This is one reason to prefer using the first detectable deviation from baseline for calibration. A second reason comes from the principle that the same method for the determination of the onset should be used for the calibration and the actual measurement on alloys. Alloys usually have a melting range and, therefore, do not melt with a linear section of the DTA curve. Thus, the onset for alloy melting is better taken using the first detectable deviation method. With these points in mind, it makes sense to use the first detectable deviation from baseline method for the calibration With the use of computers for recording the thermocouple voltages, instrument manufacturers introduced software for the analysis of the DTA curves and determination of the reaction temperatures. In most cases, the software uses the extrapolation method for the determination of the temperature T_T^{extrap} instead of $T_T^{onset.}$

2.4 Quantitative Enthalpy and Heat Capacity Calibration

In order to determine the quantitative heat flux, the difference signal (T) must be converted to one of energy units by a calibration process. The method uses the heat of a specific transformation per unit mass in a standard sample, such as heat of fusion ($H_{standard}$) and the sample mass, $M_{standard}$. The instrument sensitivity coefficient, S, at various temperatures is determined from the ratio obtained from melting a series of standards (usually pure metals).

$$S = M_{standard}\,H_{standard}/\int T dt$$

The integral is the area of the peak deviation from the baseline determined from a plot of T versus time. Alternately, the original voltage difference from the thermocouples can be used instead of the temperature. The quantity m standard, H standard is the product of the mass of the standard and the heat of fusion per unit mass. Thus, for an unknown sample,

$$M_{standard}\,H_{standard} = \int T{*}S dt$$

where S may be interpolated between the two standards spanning the temperature rnge of interest. The calibration is often performed by the instrument software and converts the DTA signal area from units of milli-volt seconds or Kelvin seconds to Joules. In order to obtain accurate heat-flux information, the same heating/cooling rate, gas flow rate, sample/reference cups, and temperature range should be employed for standard and unknown. After conversion of the DTA signal to energy, some instruments provide a second calibration to directly provide heat capacity measurement. For many heat-flux DSC instruments, heat capacity calibration is done by software with data obtained by performing a heating scan with a pair of empty cups, to get the baseline, and performing a second heating scan with the chosen reference material in one cup and an empty second cup.

So for **cobalt chloride** we consider all the values can calculate as:

T_m = 999k
S=0.05
$M_{standard}$ = 0.129839kg/mol
a = 0.03
$T_{T,c}$ = 293k
$T_{w,cp}$ = 297k
$T_{s,cp}$ =298k
$T_{s,c}$ =298k
$T_{w,c}$ = 295k
$T_T^{onset} = T_m + a\ (t_{s,cp} - t_{T,c})$

$T_T^{Extrap} = T_m + a\ [t_{s,c}\ (t_{s,cp} + t_{w,cp} + t_{w,,c})/(\ t_{s,c} + t_{w,,c})]$
T_T^{onset} = 999 + 0.03(298 – 293) = 999 + 0.15 = 999.15K

T_T^{Extrap} = 999 + 0.03 [298 (298 + 293 + 295)/ (298 + 295)]
= 999 + 13.38 = 1012.38739 K
$T_{peak} = T_T^{Extrap} - T_T^{onset}$ = 1012.38 - 999.15 = 13.15K

As we know that
$S = M_{standard}\ H_{standard}/\int Tdt\ \{\ \int Tdt = T_{peak}\ \}$

$H_{standard} = T_{peak}*S/\ M_{standard}$
$H_{standard}$ = 0.05*13.15/0.129838 = 5.996KJ/mol

So for **Nickel chloride** we consider all the values can calculate as:

T_m = 1274k
$M_{standard}$ = 0.1295994kg/mol
a = 0.21
$T_{T,c}$ = 293k
$T_{w,cp}$ = 297k
$T_{s,cp}$ =298k
$T_{s,c}$ =298k
$T_{w,c}$ = 295k
S = 0.05
$T_T^{onset} = T_m + a\ (t_{s,cp} - t_{T,c})$

$T_T^{Extrap} = T_m + a\ [t_{s,c}\ (t_{s,cp} + t_{w,cp} + t_{w,,c})/(\ t_{s,c} + t_{w,,c})]$

T_T^{onset} = 1274 + 0.21(298 – 293) = 1274 + 1.05 = 1275.05K

T_T^{Extrap} = 1274 + 0.21 [298 (298 + 293 + 295)/ (298 + 295)]
= 1274 + 93.66 = 1367.66 K
$T_{peak} = T_T^{Extrap} - T_T^{onset}$ = 1367.66 – 1275.05 = 92.61K

As we know that
$S = M_{standard}\ H_{standard}/\int Tdt\ \{\ \int Tdt = T_{peak}\ \}$
$H_{standard} = T_{peak}*S/\ M_{standard}$
$H_{standard}$ = 0.05*92.61/0.129599 = 35.72 KJ/mol

As we compared Heat of Evolution of Cobalt Chloride and Nickel Chloride, Nickel Chloride is much higher than Cobalt Chloride. We can calculate the ratio of heat of evolution and get the value of any other metal Heat of evolution with this constant.

3. Conclusion

As we show here that standard heat of evolution of Nickel Chloride is almost 6 times of Cobalt Chloride. Melting Point of Nickel Chloride is 1.5 Times of Cobalt Chloride. But The ratio of standard Heat of Evolution shown as Calorimetry Constant and here calorimetry constant is almost 6. So According to result as shown that Nickel chloride is almost 6 times better than for heat of evolution. For any aircraft we can use cobalt chloride with coating nickel chloride. with the coating of Nickel chloride a material of cobalt chloride is light weighted and used in many automobile material and increases melting point and heat of evolution with the help of Nickel Chloride coating lamination.

$K_c = H_{standard,\ cobalt}\ /\ H_{standard,\ Nickel}$
Here K_c is 0.16.

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