Meteorites
Vol. 3, Nos. 1–2, 2014, 33–44
www.meteorites.pwr.wroc.pl
DOI 10.5277/met140103

NWA 6255 METEORITE – THERMOPHYSICAL PROPERTIES OF INTERIOR AND THE CRUST

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Abstract: Differences in the thermophysical properties of NWA 6255 meteorite samples obtained from various locations with respect to the distance from the surface of the meteorite were evaluated by a differential scanning calorimetry (DSC). DSC is a perfect tool to experimentally verify theoretically predicted thermophysical properties of extraterrestrial matter. The specific heat capacity of the crust and the interior of meteorite were determined to be in the temperature range of 223−823 K. Measured *Cp* values at room temperature for crust and for the interior of this meteorite were 602 and 668 $J \cdot kg^{-1} \cdot K^{-1}$, respectively. In addition, the phase transition of troilite from: (a) the fusion crust samples, (b) the edge part of the meteorite (1−2 mm below the crust), and (c) the interior (over 10 mm below the fusion crust) was examined. It is shown that the shift of α/β transition peak of the troilite exhibits the temperature gradient evolved during atmospheric passage of a meteoroid. Moreover, the enthalpy changes of α/β transition were used to determine the troilite content in the meteorite samples (3.6 wt.%). Obtained data are in agreement with previous Leco method's results, since NWA 6255 is relatively fresh find (W1) and troilite tends to oxidized quickly.

Keywords: NWA 6255, DSC, thermophysical properties of meteorite, specific heat capacity, troilite phase transition, troilite cosmothermometer

INTRODUCTION

The NWA 6255 meteorite was found in Morocco in 2009. The exact place of find and the coordinates are unknown, so the meteorite belongs to a large group of meteorites represented under the dense collection area name "North West Africa (NWA)" and was registered under the number of 6255 (it was 6255th meteorite from the region to be classified and assigned a number). The total mass of the two pieces of NWA 6255 was 3.2 kg. It was classified as an L-type ordinary chondrite, due to its low metal content with the petrographic type L5, shock stage S4, and weathering grade of W1 (www.lpi.usra.edu, 2014).

NWA 6255 is an interesting meteorite not only because it is really fresh (Fig. 1), unique or especially distinctive object, but also because it is a very common meteorite type. It is one of 5565 approved meteorites, classified as L5 type chondrite (www.lpi.usra.edu, 2014), and therefore representative of typical S-type asteroid material (Sears, 2004).

The bulk chemical composition of NWA 6255 has been previously analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP MS) (Łuszczek, 2012) and the content of volatile elements, such as sulphur was determined by the Leco method. It was found that NWA 6255 contains ca. 1.65 ± 0.02% of sulphur. This indicates that the meteorite may have sufficient content of troilite (FeS) for precise determination of its thermophysical transitions. Since NWA 6255 is a relatively fresh desert find and considering the fact that troilite is prone to relatively fast oxidation (Velbel, 2014), the meteorite is a good representative rock of its L-chondrite parent body. NWA 6255 was not evaluated in terms of thermophysical properties before.

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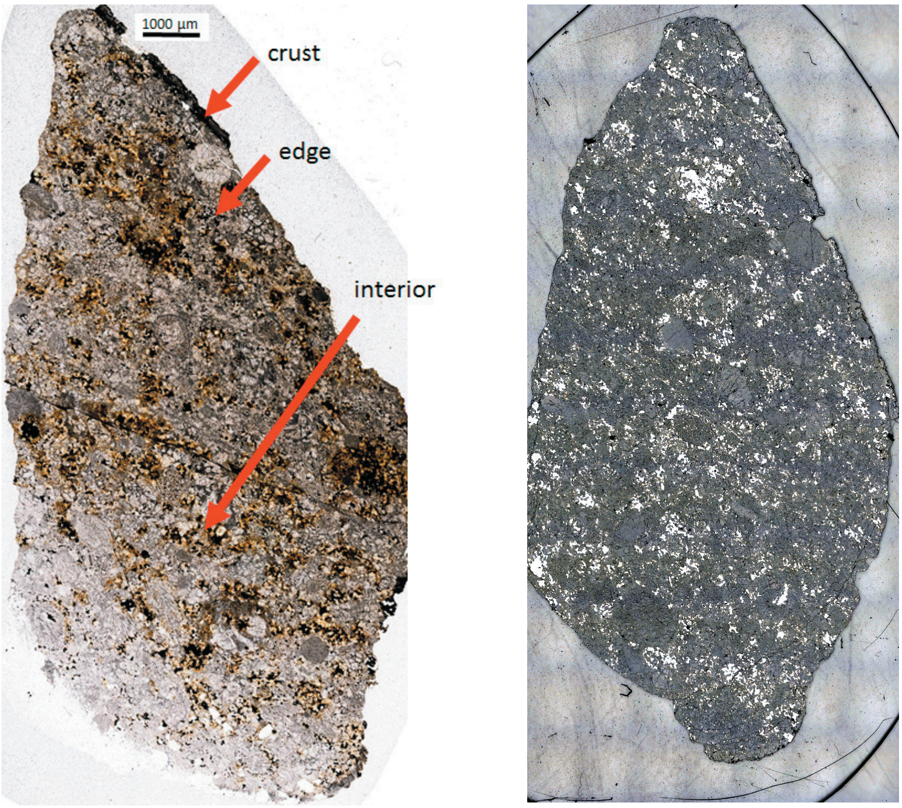

Fig. 1. Microscopic view of NWA 6255 chondrite; transmitted (left picture) and reflected light (right picture)

Thermophysical properties data of meteorites can seldom be found in the literature. However, as they represent principal features of the extraterrestrial matter it is fundamental to identify them. Knowledge of thermophysical properties of meteorites is extremely important for modeling the cooling rate of their parent bodies after accretion and the heat flow resulting from the decay of short-lived isotopes, mainly ^{26}Al.

The Yarkovsky and YORP (Yarkovsky-O'Keefe-Radzievskii-Paddack) effects on asteroid orbital and spin perturbations depends on the inverse thermal inertia, which varies with the square root of thermal conductivity and heat capacity. Thermal properties of meteorites, besides their importance for modelers, also provide important information on the meteorite's composition and its physical state (Opeil et. al, 2011). In many cases to date thermophysical properties were estimated and not measured directly (Gosh & McSween, 1999; Henke et al., 2012). In addition, the temperature of α/β transition of troilite (T_{α}), a mineral regularly present in ordinary chondrites in a few wt.% (ca. 5 wt.%), reflects its thermal history (Allton et al., 1993). Due to this fact, the troilite transition was proposed to be used as cosmothermometer (Lauer & Gooding, 1996) based on shift of the peak temperature indicating α/β transition of troilite.

Significant efforts have been made to determine thermal properties of meteorites, representing rocks on their parent bodies, in recent years by Szurgot (2003; 2011a, b; 2012a, b, c, d), and Szurgot and co-workers (Szurgot et al., 2008; Szurgot & Wojtatowicz, 2011; Szurgot & Polański, 2011; Szurgot et al., 2012). Valuable research was also conducted in Japanese and American laboratories by Matusi & Osako (1979), Yomogida & Matsui (1981, 1983), Gosh & Mc Sween (1999), Beach et al. (2009), Opeil et al. (2011), Consolmagno et al. (2013).

The aim of this study was to apply differential scanning calorimetry to evaluate thermal properties of NWA 6255 meteorite, especially to determine specific heat capacity and analyze troilite phase transition in various locations in the meteorite bulk, and to determine troilite content. Through investigations of meteorite fragments selected from different locations of the meteorite cross-section (Fig. 1), we expected to identify differences in troilite α/β transition, which can provide evidence of a temperature gradient generated during its atmospheric passage. To date, troilite α/β transitions have been measured only by thermoluminescence method and only for a few meteorites (Vaz, 1971, 1972; Sears, 1975). It is important to know the thermal effect (heating) that develops during entry, e.g. for estimating bolide brightness, and consequently its impact on the Earth surface, as a function of the meteoroid size.

PHASE TRANSITIONS OF TROILITE

Troilite is a nonmagnetic iron sulfide (FeS) and belongs to the pyrrhotite group. It was first discovered in 1766 in a meteorite (Albareto), and later in terrestrial rock. The name of this common extraterrestrial mineral is derived from the name of the discoverer, Italian scientist Domenico Troili (www.mindat.org, 2014).

A great deal of work has gone into discovering the nature of this mineral. FeS adopts three distinct temperature-dependent crystallographic and magnetic structures (Fig. 2) in which the Fe atoms occupy octahedral positions with varying degrees of distortion. Hexagonal troilite with space group $P\bar{6}2c$ is stable at low temperatures (Evans, 1970). In this structure, which has only been reported so far for FeS (King & Prewitt, 1982), all Fe atoms are combined in triangular clusters of three atoms in planes perpendicular to *c*. Half of the Fe-Fe bonds along *c* are parallel, whereas half are inclined to the *c* axis. Sulfur atoms may be regarded as forming triangles about these Fe-Fe bonds. The normals to the planes of these triangles tend to align with the Fe-Fe bonds; thus, half of the planes are perpendicular to *c* and half are tilted (Kruse, 1992). The structure can be derived from the NiAs structure. Based on the NiAs subcell axes $\underline{A}$ and C, the troilite supercell axes are given as $a = \sqrt{3A}$ and $c = 2C$ (Hägg & Sucksdorff, 1933).

At the α transition (named also α/β transition), the troilite structure, including its clusters, break down. Troilite transforms into the orthorhombic MnP-type structure with space group *Pnma* on the heating trough T_α (King & Prewitt, 1982). In this structure the Fe-Fe bonds form zigzag chains and all S triangles are tilted. Various values of T_α have been reported for ambient pressure: 413 K, based on electrical resistivity measurements on synthetic FeS (Ozawa & Anzai, 1966); 425 K based on DTA of syntetic samples (Moldenhauer & Brückner, 1976); and 388–423 K, according to TEM of meteoritic troilite (Töpel-Schadt & Müller, 1982).

However, Haraldsen (1941) found X-ray supercell reflections of synthetic samples to be weaker at 375 K than at 293 K. Thus, the α transition is indicated to be gradual with an onset detectable at 375 K. Kruse and Ericsson (1988) obtained a completed transition at 413 K on heating, using Mössbauer spectroscopy with meteoritic troilite. The reverse transition started at 410 K and was not completed even after 15 d of slow cooling to 280 K, where 20% of the Fe still was included in the MnP-type structure (Kruse, 1992).

Susceptibility measurements on a synthetic $Fe_{0.996}S$ single crystal by Horwood and coworkers (1976) showed that antiferromagnetically coupled spins of the Fe atoms point along the *c* axis of the NiAs subcell (c_{NiAs}) below the spin-flip temperature ($T_s \approx 445$ K), where the spin flipped reversibly by 90°. Values for T_s, include 458 K for synthetic FeS using neutron diffraction (Andresen & Torbo, 1967) and the intervals 410–470 K (heating) and 450–360 K (cooling) for meteoritic troilite (Kruse & Ericsson, 1988); the specific behavior depended on the sample pretreatment.

On heating at 483 K FeS transforms into the NiAs-type structure with the space group $P6_3/mmc$ (Fig. 2) (Töpel-Schadt & Müller, 1982), where the Fe-Fe bonds form a straight line along *c*; all S triangle planes are perpendicular to *c*. At $T_N \approx 600$ K the antiferromagnetic order in FeS breaks down into paramagnetism (Horwood et al., 1976).

Despite the voluminous literature on iron sulfides in meteorites, quantitative information on FeS properties above room temperature is rather rare. Troilite undergoes two phase transitions upon heating to the temperature below its melting point (Allton et al., 1993). Besides α/β there is a β/γ transition, which occurs at 598 ± 3 K (Chase et al., 1985).

The experimentally measured α/β onset temperature shows a systematic decline with the maximum experienced temperature, suggesting that high onset temperature is indicative of only low temperature in the natural history of the troilite samples (Allton et al., 1993). That trend is at least quantitatively consistent with the petrographic rankings of the meteorites in which troilite from the relatively unmetamorphosed L3 chondrites show a higher onset temperature than the troilite from either a highly metamorphosed L7 or an iron octrahedrite (Allton et al., 1993). Troilite was proposed to be a cosmothermometer for this reason.

The purpose of the present work was also to use troilite as the cosmothermometer and investigate the effect of temperature produced during atmospheric passage. Therefore, troilite α/β transitions in samples from different parts of the meteorite were investigated.

$$\boldsymbol{P\bar{6}2c} \xrightleftharpoons[388-423\text{K}]{\alpha/\beta\ \text{transition}} \boldsymbol{Pmcn} \xrightleftharpoons{\approx 488\text{K}} \boldsymbol{P6_3/mmc}$$

Fig. 2. Sequences of transitions of crystal structure observed in troilite from subsolidus phase (Töpel-Schadt & Müller, 1982; adapted by authors)

METHODOLOGY

A thermoanalytical technique of differential scanning calorimetry (DSC) is commonly used for following a phenomenon or a reaction occurring in a specimen that is accompanied by a change in its enthalpy whether temporal or permanent. DSC measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature in a controlled manner. The measurements provide qualitative and quantitative information about physical and chemical changes that involve exothermic or endothermic processes or changes in heat capacity (Höhne et al., 1996). The technique is regularly utilized for polymers, textiles, food, adhesives, composites, packaging and for many other materials. Beside evaluation of thermal effects of various chemical reactions, the most general physical phenomena or material properties that can be determined with DSC include physical phase transitions and specific heat capacity of a specimen. Melting, crystallization, boiling, and glass transition (for polymers) are the primary examples of applications of the DSC technique.

All measurements were conducted with a Differential Scanning Calorimeter (Q200 TA Instruments). The instrument used was a heat flux type; the power compensation method (temperature of specimen and a reference should be the same) underlay the other common DSC type. In the heat flux DSC, two thermocouple integrated sensors in a furnace allow a sample pan (crucible) and the reference pan (usually empty) placed on them (Fig. 3) to be simultaneously heated/cooled at the same rate. Absolute temperatures of both are recorded in real time. Due to the heat capacity of the examined material the sample pan temperature is a bit lower (in the heating mode) or delayed with respect to the empty reference pan. At a constant heating rate the temperature increases linearly, in parallel for two pans – the difference, ΔT can be translated into heat flow due to performed calibration.

The instrument was calibrated for both temperature and heat flow using respectively indium (melting temperature 429.75 K) and the synthetic sapphire standard with well characterized *Cp* in the broad range of temperatures.

$$\Delta H = Cp_{sp}\, \Delta T \qquad (1)$$

ΔH – measured heat flow rate
Cp_{sp} – a specific heat capacity of sapphire
ΔT – measured heating rate

Sample preparation

DSC measurements can determine thermal properties of relatively small samples of even a few mg (for chondrites it will be ca. 1.0–1.5 mm^3 for troilite phase transition, and ca. 5 mm^3 for *Cp* determination), therefore one can get information on the variation of measured property as a function of locations of a particular portion of the specimen. Sampling every mm is possible for precisely cut samples. However, this is also the main drawback of this method since a small sample mass requires multiple measurements in order to get an indication of the complete specimen. This is especially important when the specimen is heterogeneous in mm scale, like in ordinary chondrites. Therefore, while examining the chondritic meteorite with respect to troilite transitions or specific heat capacity, evaluation of few samples from all selected locations in essential. Another way to solve the problem of heterogeneity is by grinding a bigger piece of chondritic rock in order to homogenize it. Moreover, grinding has another advantage – the influence of physical state of the rock (porosity) is neglected, thus enabling instant heat transfer.

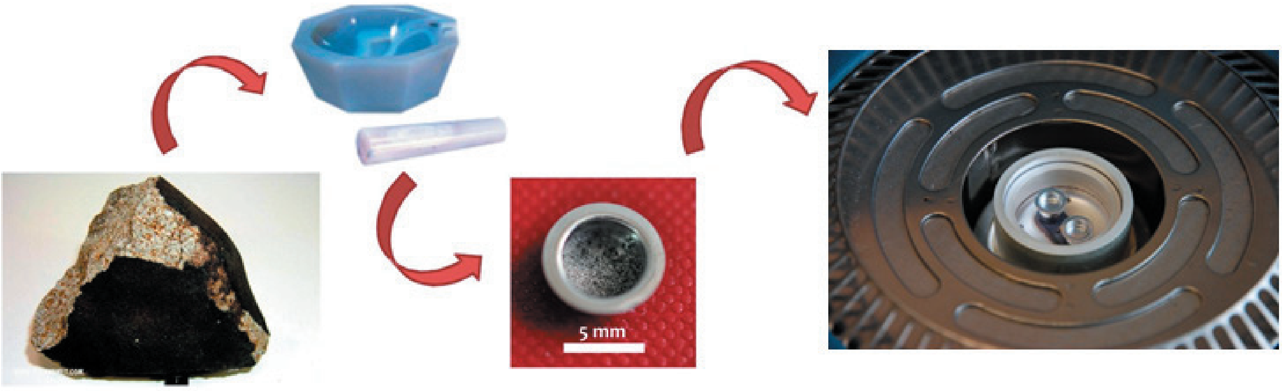

Fig. 3. Samples preparation for DSC measurements: choosing the crust, edge and interior part of meteorite (left), grinding the selected part in the agate mortar (middle top), preparing 5 mg of homogenized sample in the pan (middle bottom), putting the pan in the DSC – left pan with reference material, right with sample (right)

EXPERIMENTAL

Specific heat capacity

Specific heat capacity, *Cp* of two samples, representing the fusion crust, and the interior was determined. In DSC measurements of *Cp* of NWA 6255 samples the following equation applies:

$$C_p = C_{p_{sp}} \frac{H}{H_{sp}} \frac{m_{sp}}{m_m} \quad (2)$$

where Cp_{sp} is a specific heat capacity of the sapphire standard at a particular temperature, m_{sp} is the mass of the sapphire standard, and H is the heat flow of the meteorite specimen. Samples, with approximately the same mass as the sapphire (ca. 20 mg of grounded matter), were sealed in aluminum pans and analyzed in the temperature range between 223 and 823 K at a heating rate of 20 K·min^{-1} under nitrogen flow of 50 ml·min^{-1}. In the current investigations relative error in the measurement of *Cp* of NWA 6255 meteorites was 3–4%.

α/β phase transition of troilite

If the sample undergoes thermal transition, the measured heat flow rate momentarily changes at the endothermal α/β transition of troilite. Seven samples (with mass ca. 5–6 mg) from different parts of the meteorite were selected: three from the fusion crust, two comprising of the fusion crust and the edge of the meteorite (1–2 mm below the crust) and two from the interior of the meteorite (10 mm below the crust). They were analyzed in temperature range of 373 to 473 K to observe the α/β phase transition (Fig. 4). The conditions of the experiment, except the temperature range and the sample mass, were the same as for the measurement of the specific heat capacity. The α/β and β/γ phase transitions are also recorded during *Cp* measurements. In principle, examination of samples with lower sample mass provides more accurate results in precise determination of temperature transition T_α. This correlates with the contact area of the samples with the bottom of the crucible, which greatly influences the speed of response. In samples of higher mass, where the entire specimen cannot connect with the bottom of the crucible, detection of a thermal effect is delayed, or unsatisfactory in resolution (wider) due to prolonged heat transfer through a bulky specimen. In this work we focused on the α/β transition due to its importance as a cosmothermometer.

RESULTS

Specific heat capacity

The heat capacity of two samples from different regions: one from the crust, and one from the interior was determined. The mass of the samples was 20.3 and 20.9 mg, respectively. Table 1 compiled, calculated with equation 2, *Cp* of these samples at various temperatures. Temperature 423 K is omitted because of the α/β phase transition of troilite occurs in this region displaying endothermic heat effect disturbing proper determination of the *Cp*.

The values of *Cp* for the interior are higher than those for the crust. An increase of *Cp* value with the increase of temperature was observed for both samples. However, from 393 K the *Cp* for the interior in-

Table 1. Specific heat capacity *Cp* [J·kg^{-1}·K^{-1}] of NWA 6255 meteorite samples at various temperatures

T [K]	T [°C]	*Cp*	
		crust	interior
223	–50	476	532
263	–10	546	607
283	10	577	641
300	27	602	668
323	50	634	705
373	100	701	784
398	125	740	840
448	175	759	862
473	200	774	880
523	250	805	929
573	300	830	965
623	350	842	986
673	400	855	997
723	450	868	1007
773	500	876	1008
823	550	–	1017

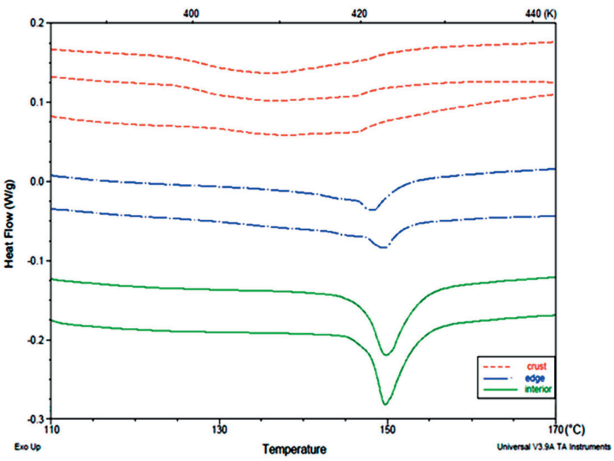

Fig. 4. Endothermic peaks of α/β transition of troilite from different parts of the NWA 6255 meteorite. DSC scan showing the heat flow during heating of the meteorite samples (dash line – crust, dash dot line – edge, solid line – interior)

creases a bit more steeply than for the crust (Fig. 5). From 573 K for the crust, and from 623 K for the interior the increase rate of *Cp* become slower, only about 10 J·kg^{-1}·K^{-1} for 50 K.

α/β transition

Figure 4 shows the heat flow during heating of the meteorite samples. An intense endothermic peak indicates α/β phase transition of troilite. The enthalpy changes $\Delta H_{\alpha/\beta}$ and the onset of T_α were determined by using the TA Analysis software (dedicated to DSC of TA Instruments). The $\Delta H_{\alpha/\beta}$ is calculated as the area under the peak, whereas the peak temperature is regarded as the temperature of α/β phase transition.

The masses of analyzed samples, the temperature transition and the transition enthalpy are shown in Table 2. The average value and standard deviation were calculated for specimens of crust, edge and interior of the meteorite.

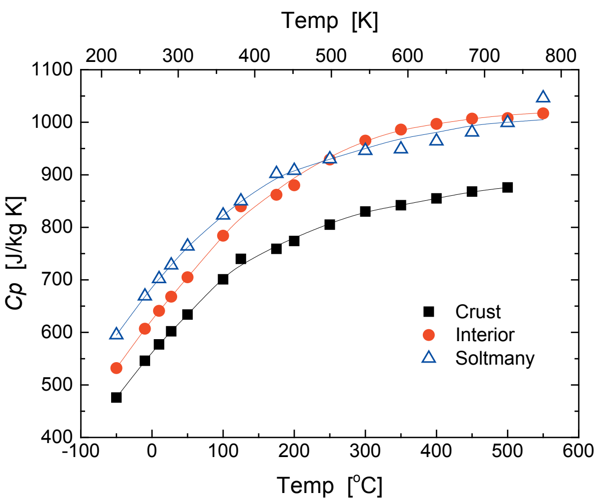

Fig. 5. *Cp*(*T*) dependence for crust and interior of NWA 6255 in comparison with bulk of Sołtmany (Szurgot et al., 2012)

Temperature of α/β transition of troilite in the meteorite exhibits an increase, from the crust (ca. 414.4 K) inward, through the edge, 1–2 mm part below the crust (422.25 K) to the interior (ca. 422.9 K). Despite small difference in T_α between the edge and the interior it becomes obvious that the edge has different characteristics than the interior when comparing offset temperature (T_{off}). T_{off} indicates the early stage of the transition or, as in this case, presence of various crystallographic types of the troilite. The T_{off} of the edge is 1.4 K less than that of the interior.

Despite the fact that the T_α of the edge differs slightly as compared to the interior, significant changes of enthalpy ($\Delta H_{\alpha/\beta}$) are observed. Therefore, the content of FeS in the edge part of the same crystallographic form as in the interior is three times lower than in the interior. The edge experienced rapid but intense elevation of temperature during atmospheric passage.

Troilite concentration

Troilite content in chondrites is about 5 wt.% (Hutchison, 2006; McSween & Huss, 2010). Our preliminary data on the bulk chemical composition established by Leco method indicate that NWA 6255 contains about 1.65 ± 0.02 wt.% of sulphur (Łuszczek, 2012). Knowing the molar mass of troilite (m_{molFeS} = 87.91) and that sulphur constitutes 36.5% in FeS, and assuming that the all sulphur crystallized in the form of FeS troilite, we calculated the troilite content in NWA 6255 samples to be ca. 4.5 wt.%.

We can compare the results obtained by Leco method with that from DSC measurements. The $\Delta H_{\alpha/\beta}$ of the interior part is representative, as the interior of the meteorite was not changed by either the temperature experienced during atmospheric passage, or the weathering of the meteorite after fall. The mean enthalpy change determined for α/β transition

Table 2. Temperature of α/β transition (the T_{off} is an offset temperature), transition enthalpy and estimation of FeS content of samples from different part of NWA 6255 meteorite

part of meteorite	mass [mg]	T_{off} [K]	mean T_{off} (SD)	T_α [K]	mean T_α (SD)	$\Delta H_{\alpha/\beta}$ [J·g^{-1}]	mean $\Delta H_{\alpha/\beta}$ (SD)	FeS content [%]	mean FeS content [%]
crust	5.4	-	-	410.25*	414.4 (3.52)	0.44	0.44 (0.06)	1.0	1.0 (0.12)
	5.2	-		414.15*		0.37		0.9	
	3.7	-		418.85*		0.51		1.2	
edge	5.5	418.35	418.9 (0.55)	421.55	422.25 (0.7)	0.55	0.50 (0.06)	1.3	1.15 (0.15)
	6.1	419.45		422.95		0.44		1.0	
interior	5.7	419.95	420.3 (0.35)	422.95	422.9 (0.5)	1.57	1.53 (0.04)	3.7	3.6 (0.1)
	5.1	420.65		422.85		1.49		3.5	

* Peak positions were determined at temperatures between 410 to 418.85 K however, for these samples there was a broad depression indicating two effects of partially oxidized troilite and its *α/β* transition combined.

(1.53 $J{\cdot}g^{-1}$) shows that troilite is present in NWA 6255 as a small fraction of the overall mass.

We estimated the mean troilite content in the samples by measuring enthalpy change for the α/β transition. According to Allton and co-workers, enthalpy change for α/β transition of troilite is equal to 42.5 $J{\cdot}g^{-1}$ at transition temperature 423 K (Allton et al., 1994), i.e. at the mean transition temperature established for the NWA 6255 meteorite. Therefore, based on measurements of the interior, the content of troilite was estimated to be 3.6 wt.%. Current estimation of troilite content seems to be correct since values of enthalpy changes 1.49–1.57 $J{\cdot}g^{-1}$ are in agreement with those obtained by Lauer and Gooding (1996).

Moreover, the enthalpy of the fusion crust is much lower in the case of the edge as compared with that of the interior part. The lower value of $\Delta H_{\alpha/\beta}$ indicates that the sample contains less troilite. Therefore, troilite content in the crust part is much lower than in the interior. The range of troilite content is, however, much broader, between 0.9 and 3.7 wt.% (Tab. 2). It should be added that results obtained based on DSC measurements determined only the troilite in the crystallographic form undergoing α/β transition.

DISCUSSION

Thermophysical properties of the specific heat capacity and the temperature of α/β phase transition of troilite of the interior and the crust of NWA 6255 meteorite were determined by means of DSC measurements and are presented in this paper. The results for the fusion crust, the edge of the meteorite (1–2 mm below the crust), and for the meteorite interior (10 mm below the crust) were compared. By using small samples obtained from various locations in the meteorite, we are able to determine how the thermophysical properties change with respect to the sample location and the heating it experienced during atmospheric passage.

Heat capacity

The values of *Cp* of ordinary chondrites are similar to terrestrial rocks, thus proving the uniformity of mineral composition of the matter constituting the universe. The assumption that the heat capacity of a rock sample equals the sum of *Cp* of constituent minerals with respect to their weight fractions (Gosh & McSween, 1999) was supported by Opeil and co-authors (2011). Consequently, theoretical calculations of heat capacity can be directly compared with the experimentally obtained values of *Cp*, based for instance on DSC measurements. Using theoretical data of the constituent minerals of ordinary chondrites to calculate total heat capacity of a sample gave results that correspond well with experimentally determined values (Opeil et al., 2011 after Yomogida and Matsui, 1983). Calculation of *Cp* for Braunschweig (L6) based on *Cp* values of constituting minerals gave reliable values of *Cp* for this meteorite (704 ± 20 $J{\cdot}kg^{-1}{\cdot}K^{-1}$) at room temperature (Szurgot et al., 2014). They are nearly identical with the experimental values of *Cp* = 682 ± 15 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ measured by DSC (Szurgot et al., 2014). Similary, the theoretical calculation of *Cp* for Sołtmany (L6) at room temperature (674 $J{\cdot}kg^{-1}{\cdot}K^{-1}$) (Szurgot, 2014) is close to the experimental values of *Cp* = 671 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ (Wach et al., 2013). Moreover, results presented in this paper for NWA 6255 (*Cp* = 668 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ at room temperature) show good agreement with theoretically predicted value of *Cp* for L group chondrites (*Cp* ≈ 700 $J{\cdot}kg^{-1}{\cdot}K^{-1}$) (Gosh & McSween, 1999).

As specific heat capacity is the inherent property of the matter, the results obtained experimentally by DSC measurements may be used to more accurately model the thermal history of asteroids as well as predict their future state. The heat capacity should be determined at various temperatures as the *Cp* is temperature-related. Moreover, *Cp* depends of the chemical composition of the sample, and since the interior and the crust have different composition, this should be measured for specimens obtained from various locations of the meteorite with respect to the distance from its surface. Therefore, measuring the samples from different places in the meteorite cross-section provides valuable data. It may be a useful tool for determining the heat gradient in the meteorite during its atmospheric passage. In fact, to come to more precise conclusion the exact distance from the fusion crust should be known. It will also be pivotal to estimate the chemical and the mineralogical composition of each sample as the *Cp* value depends on both. This will also influence the temperature of the troilite transition, T_α. Karwowski (2012) performed interesting work reporting the mineralogical composition of the fusion crust for an analogous chondrite, the Sołtmany (L6) meteorite. There is a need for similar examination of NWA 6255 (and other meteorites) in order to verify the conclusions.

About 80% of a meteoroid composed of an ordinary chondrite is lost during atmospheric entry. This loss was proven by measurements of $^{22}Ne/^{21}Ne$ isotopic ratio which then enabled the pre-atmospheric radius of a meteoroid (Bhandari et al., 1980) to be estimated. It is well known that refractory elements tend to survive high temperatures, whereas volatile elements are the first to be mobilized firstly as the temperature increases. Therefore, the refractory elements are mostly to remain in the fusion crust. Refractory elements are in most cases also siderophile or chalckophile elements (from a geological point of view), so they will substitute in Fe-Ni alloy or in sulfides. Sulfides have a lower melting temperature compared to metals alloys, so they tend to sublimate from the outer region of the fusion crust (Karwowski, 2012). Elements such as metals will decrease the specific heat capacity value (Waples & Waples, 2004). Enrichment of the crust with metals may explain why the *Cp* value of the crust is lower, over the entire measured temperature range, than for the interior of the NWA 6255 meteorite.

Water bonded in the hydroxide group influences the specific heat capacity in an opposite way than metals. It will increase the *Cp* value, as water has one of the highest *Cp* value (Waples & Waples, 2004). Water is only present in asteroids beyond the snow line, in the outer part of the asteroid belt orbits, such as carbonaceous asteroids with water-rich, clay-like minerals. By contrast, ordinary chondrites originated from the inner part of the asteroid belt dominated by rocky, siliceous and dry bodies (Lang, 2011). Nevertheless, due to the fact that ordinary chondrites come from the region of the Solar System where water is absent, this consideration should be neglected.

Data of experimentally determined *Cp* values at room temperature of L-chondrites are listed in Table 3. Results obtained in this work are in good agreement with Alexeyeva's data (1958) for Kharhov (L6), but lower than for Elenovka (L5). The *Cp* value for Kukschin is much higher than that for NWA 6255 and also exceeds the theoretical value of *Cp* for L-chondrites of 700 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ (Ghosh & McSween, 1999) or 770 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ (Matsui & Osako, 1979). It is well known that specific heat is related to the content of metallic and sulfide minerals. So the differences exhibited in *Cp* values of Kukschin (Alexeyeva, 1958) are probably due to the differences in the mineral composition of the measured samples. On the other hand, the Y-74191 has very low *Cp*, which may be due to the fact that smaller sample evaluated (m = 10 mg) might not have been representative of the complete meteorite mass as the experimental value of *Cp* does not meet the theoretical value for L group chondrites. Currently obtained results of *Cp* are in the same range as those for Sołtmany (L6) and Braunschweig (L6).

Table 3. Heat capacity of L group chondrites at room temperature

meteorite	type	*Cp* $J{\cdot}kg^{-1}{\cdot}K^{-1}$	source
Kukschin	L6	1000	Alexeyeva (1958)
Kharhov	L6	707	Alexeyeva (1958)
Elenovka	L5	762	Alexeyeva (1958)
Yamoto-74191	L3	603	Matsui & Osako (1979)
Sołtmany	L6	671	Wach et al. (2013)
		705–769	Szurgot et al. (2012)
Braunschweig	L6	682	Szurgot et al. (2014)
NWA 6255	L5	668	this work

The comparison of heat capacity values at various temperature of NWA 6255 with Sołtmany (Szurgot et al., 2012) is depicted in Fig. 5. In the temperature range of 223–523 K, the *Cp* values of Sołtmany are slightly higher (ca. 40–50 $J{\cdot}kg^{-1}{\cdot}K^{-1}$) than these for the interior samples of NWA 6255. However, over 523 K the heat capacity of both meteorites are nearly identical (within experimental error). Since the masses of the samples of both meteorites are similar, and the procedure to determine the *Cp* values is exactly the same, the differences in *Cp* values may reflect heterogeneity in mineral and chemical composition of both meteorites.

α/β transition

The enthalpy of α/β transition could be used to estimate the troilite content in the sample (Szurgot et al., 2012). After heating of the samples containing troilite, the thermal effect ($\Delta H_{\alpha/\beta}$) of α/β transition is reduced and the peak of the transition shifts to a lower temperature. This fact is not surprising as the T_α depends on the relict temperature that the material experienced during its thermal history (Allton et al., 1993). It is known that T_α is inversely proportional to the relict temperature of troilite. The current results are in good agreement with this consideration, as the lowest values of T_α for crust (Tab. 2) show the evidence of the highest temperature experienced during atmospheric passage. However, differences in T_α with regards to the distance from the meteorite surface inward provides evidence that the meteoroid experienced increased temperatures due to friction in the atmosphere as well as heat flow. Sampling the cross-section of a meteorite from crust to the interior (precisely defined fractions) may give valuable information. Therefore, differences in temperature of α/β transition of troilite, as a representative constituent, in crust, edge and interior of NWA 6255 (Tab. 2) indicate the temperature gradient that the meteorite experienced. Accurate data representing thermophysical characteristics of a meteorite or its parent body can be obtained only by examination of a fresh fall as troilite tends to oxidize quickly.

The reduction of thermal effects is dependent on both the temperature experienced and the time of heating. The crust reaches its maximum temperature during atmospheric passage, after which bubbles and pores are observed due to the evaporation of sulfides (Karwowski, 2012). Thus, troilite content (also that in its crystallographic form displaying α/β transition) is minimal in crust. Troilite that endured an intense increase of temperature changes its structure. Obtained low values of $\Delta H_{\alpha/\beta}$ support this principle, which is also demonstrated in the lowest FeS content in the crust throughout the cross-cut of the meteorite. In the crust samples there was a broad depression in the DSC thermogram indicating two effects of partially oxidized troilite and its α/β transition combined. This is characteristic for specimens of the crust. A significant decrease in the characteristic high peak of α/β transition and its shifting to lower temperature (Fig. 4) also indicate a substantial reduction of troilite in the crust.

The edge of a meteorite is in the intermediate zone in terms of temperature produced during atmospheric friction (Vaz, 1972). Shape of thermogram, i.e. the heat flow curve for the edge is composed of the peak characteristic for α/β transition and, starting at lower temperature, depression characteristic for the crust. Therefore, the edge material is only moderately exposed to high temperature during its passage through the atmosphere. The values of $\Delta H_{\alpha/\beta}$ also indicate the thermal processing. The edge experienced rapid but intense elevation of temperature during atmospheric passage. Despite the fact that the T_α of the edge differs slightly as compared to the interior, significant changes of enthalpy ($\Delta H_{\alpha/\beta}$) are observed. Therefore, the content of FeS in the edge (present in the same crystallographic form as in the interior) is three times lower in comparison with the interior of the meteorite.

The interior of a meteorite may not experience thermal changes during atmospheric passage. Well defined peaks of α/β transition of the interior troilite of NWA 6255, a transition temperature similar to the theoretical values, and a significantly higher $\Delta H_{\alpha/\beta}$ than for the crust and edge samples support this hypothesis. The current results are in good agreement with the results of Vaz (1971, 1972) and Sears (1975) who found through TL measurements that temperatures as high as 250°C (523.15 K) have been experienced no futher than 0.5 mm from the present surface, but the materials up to about 5 mm below the crust experienced temperature rise of over 150°C (423.15 K). The lack of a shift in the α/β transition peak of the troilite indicates that the temperature of the interior (10 mm below the fusion crust) did not exceed 150°C (423.15 K).

Troilite concentration

Determined content of troilite in the NWA 6255 meteorite is in relatively good agreement with the previous results from Leco method. It should be added that the DSC measurement were conducted one year after determination of sulphur content by Leco method. This may be the reason why troilite content estimated on the basis of current thermophysical measurement is lower, as troilite tends to oxidize quickly (Velbel, 2014). Nevertheless, the value for interior with standard deviation is in the same range as that by Leco determination. These results (Tab. 2) support our opinion that NWA 6255 has a heterogeneous distribution of FeS in terms of crust, edge and interior of the meteorite. One should bear in mind that estimation of troilite content in the meteorite is only valid for the fresh fall or finds with a low weathering grade (W0−W2), where FeS did not undergo the terrestrial weathering. Moreover, it should be done for ground, homogenized samples from representative parts of the meteorite (avoid shock vein, shock melt pocket as well as part of meteorite generally enriched in metals). Troilite content should be regarded as a valuable complementary method to estimate the composition of samples since troilite constitutes a minor part of a meteorite, and the DSC instrument allows measurement of samples with relatively small masses (2−25 mg).

CONCLUSIONS

We have applied a thermal analytical technique of differential scanning calorimetry for evaluation of thermophysical properties of the ordinary chondrite NWA 6255. We also demonstrated the efficacy of DSC, a highly underrated tool, for determination of thermophysical properties of extraterrestrial rocks. Beside determination of specific heat capacity over a wide range of temperatures, the technique can provide information on thermal transitions of crystallites comprising the specimen, specifically troilite, whose extent may be correlated with the thermal history of the sample, and consequently used as the cosmothermometer, as proposed by Howard and Gooding (1996) and later developed by Szurgot. The applied technique requires that the specimen itself posses flat and thin geometry to allow instant heat transfer within the whole material. Otherwise, it is recommend to grind a complex sample to diminish the influence of porosity, cracks etc. since thermal conductivity and by extension the measured *Cp* are controlled by the physical state of the material. Grinding may be also advantageous for specimens characterized by high heterogeneity to obtain average values representative of the whole sample. Nevertheless, the measurements are usually conducted using small samples (a few mg), which depending on the specific meteorite, may have limited availability.

Detailed examination of a cross-section of the NWA 6255 meteorite revealed a gradient, along the axis from the surface to the interior, in the enthalpy of troilite transition, which reflects the thermal history of the meteorite in distinct locations. Our research proved that the natural relict temperature inferred from troilite shows values that vary systematically not only with metamorphic and shock grades of the examined samples (Allton et al., 1994) but also with the distance from the crust. As it was expected, the surface experienced the highest temperature (minor heat effect of troilite transition), whereas the site on the edge of the meteorite (1−2 mm below the crust) experienced a much lower temperature as demonstrated by a diminished peak in the DSC heat flow thermogram.

The current results obtained by the DSC can be validated by well-established methods, such as thermoluminescence, and are indeed in good agreement with those. Changes of the *Cp* with temperature were followed, and when compared to that of another chondrite showed high correlation. The *Cp* of the crust was somewhat lower than that of the meteorite's interior, which is due to relatively higher metals content, as metals and others siderophile elements tend to be refractory and so survived the high temperature during ablation.

Knowing the mineral composition and the specific heat capacity of the specimen while then taking into account the temperature and heat effect of transition of the troilite in the meteorite bulk set against, for instance, sulphur content can also provide evidence of the thermal history of the parent body of the meteorite. Therefore, the straightforward method of DSC used for determination of thermophysical properties of meteorites may provide complementary information to better understand the matter of different bodies of the Solar System.

ACKNOWLEDGEMENTS

The analyses were financed by the National Science Center of Poland, grant no. DEC-2011/03/N/ST10/05821, and the internal grant of Wrocław University of Technology "Rozwój potencjału dydaktyczno-naukowego młodej kadry akademickiej Politechniki Wrocławskiej" grant no. MK/SS/84/VI/2013/U. The authors would like to thank reviewers: G.J. Consolmagno and M. Szugot for comprehensive review of this paper and constructive notes.

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www.lpi.usra.edu, 7.04.2014.

www.mindat.org, 7.04.2014.

Publishers: Wrocław University of Technology, Faculty of Geoengineering, Mining and Geology
Polish Meteorite Society