Khwarizmi Engineering Journal, Vol. 11, No. 2, P.P. 51- 61 (2015)

Al-Khwarizmi Engineering Journal

Experimental Study of the Thermal Diffusivity and Heat Capacity Concerning Some Duplex Stainless Steel

Riad Harwill Abdul Abas[*] **Nabil Kadhim Taieh**[**]

Avesta Research Centre/ High Performance Stainless and Alloys/ Avesta/ Sweden
***Department of Mechanical Engineering/ Technical Institute/ Kut*
*Email: Riad_riri@hotmail.com
**Email: nkadom123@gmail.com

(Received 20 October 2014; accepted 10 March 2015)

Abstract

In the present work, thermal diffusivity and heat capacity measurements have been investigated in temperature range between RT and 1473 K for different duplex stainless steel supplied by Outokumpu Stainless AB, Sweden. The purpose of this study is to get a reliable thermophysical data of these alloys and to study the effect of microstructure on the thermal diffusivity and heat capacity value. Results show the ferrite content in the duplex stainless steel increased with temperature at equilibrium state. On the other hand, ferrite content increased with increasing Cr/Ni ratio and there is no significant effect of ferrite content on the thermal diffusivity value at room temperature. Furthermore, the heat capacity of all samples increases with temperature from room temperature to 473 K, while it decreases with increasing temperature until 1073 K. Then it increases with temperature at higher temperature. Curie temperature and sigma phase formation temperature can be detected by heat capacity-temperature curves.

Keywords: *Duplex Stainless Steel, Thermal Diffusivity, Thermal conductivity.*

1. Introduction

Modeling of high temperature process requires access to reliable thermophysical properties of high temperature systems that are relevant to heat and mass transfer computations. A priori estimations of the thermophysical properties have often been found to be limited to specific temperature and compositional ranges and it is still far away towards a unified picture of the structure of the system and its properties. Experimental data are needed to satisfy the requirements of internal consistency and reliability with respect to extrapolations to temperature and compositional regions beyond the range of measurements. These in turn, would necessitate accurate experimental measurements under well controlled conditions and reliable property models that extrapolate the data as functions of temperature and composition [1].

The methods for measuring the thermal diffusivity can be classified into two main groups: *viz.* periodic and nonperiodic heat flow methods. The periodic method includes Angstrom, thermoelectric and radial wave methods, while the nonperiodic method includes bar, small area, semi-infinite plate, radial heat flow high-intensity arc, electrically-heated rod and flash method.

Most of these methods have inherent limitations primarily due to heat transport via convection as well as heat loses by radiation at elevated temperatures. The impact of these factors is minimized by laser flash technique, which is one of the transient methods due to the small thickness of the sample and the high-speed heat supply to the specimen [2].

Thermal conductivity assumes a critical role in the performance of materials in high temperature applications. Low thermal conductivity values are required when the purpose is to minimize heat losses. On the other hand, when heat transfer from one location to another is desirable, materials with higher thermal conductivities must be chosen. So, reliable thermal conductivity values are essential in a selection of a material in order to get the best performance of this material in a specific application.

Thermal conductivity is the property that determines the working temperature levels of a material, and it is an important parameter in problems involving steady state heat transfer (equation 1). However, it is one of the physical quantities whose measurement is very difficult and it requires high precision in the determination of the parameters involved in its calculation.

$$\frac{\Delta Q}{\Delta t.A} = -K\,\frac{\Delta T}{\Delta X} \qquad \dots (1)$$

where;

$\Delta Q / \Delta t\ A$: Rate of heat loss per unit area (Wm^{-2}).

K: Thermal conductivity ($WK^{-1}m^{-1}$).

$\Delta T / \Delta x$: Temperature gradient (Km^{-1}).

Equation 1 is similar in form to Fick’s first law for atomic diffusion. For these expressions, K is analogous to the diffusion coefficient D, and the temperature gradient parallels the concentration gradient, dC/dx [3].

Measuring the thermal conductivity coefficient in the high temperature range is a complicated problem, because it is difficult to correctly include the heat transfer between sample and environment. In this situation, instead of measuring K, this coefficient may be found by result of measurements of the thermal diffusivity of the material (for which no measurement of heat flux required) and by the data of heat capacity Cp and density using in the relation:

$$K = Cp . \propto . \rho \qquad \dots (2)$$

Where: α=thermal diffusivity (m^2/s); k=thermal conductivity (W/m K); **ρ**=bulk density (kg/m^3) and Cp =specific heat (J/kg. K) [4].

The aim of the present work was to precisely measure the thermal diffusivity, heat capacity and thermal conductivity of some duplex stainless steel types made by Outokumpu Stainless Company in Sweden in order to get an accurate data of the thermophysical properties and to investigate the impact of microstructure and temperature on the thermophysical properties of these alloys.

2. Experimental Work

All experimental works have been done at Royal Institute of Technology, Stockholm, Sweden and at Avesta Research Centre, Avesta, Sweden.

2.1. Materials and Samples Preparation

Duplex stainless steels have a mixed microstructure of austenite and ferrite, the aim usually being to produce a 50/50 mix, although in commercial alloys the ratio may be 40/60. Duplex steels have improved strength over austenitic stainless steels and also improved resistance to localized corrosion, particularly pitting, crevice corrosion and stress corrosion cracking. They are characterized by high chromium (19–28%) and molybdenum (up to 5%) and lower nickel contents than austenitic stainless steels. The most used duplex Stainless Steel are the 2205 (22% chromium, 5% nickel) and 2507 (25% chromium, 7% nickel); the 2507 is also known as "Super duplex" due to its higher corrosion resistance. The properties of duplex stainless steels are achieved with overall lower alloy content than similar-performing super-austenitic grades, making their use cost-effective for many applications.

Five types of duplex stainless steel produced by Outokumpu Stainless AB, Sweden have been used in the present work. Table 1 presents the chemical compositions of the used materials.

Table 1,
Chemical composition of duplex stainless steel.

Sample	**Chemicals composition (wt %)**									
	C	**N**	**Cr**	**Ni**	**Mo**	**Cu**	**Ti**	**Mn**	**Si**	**Co**
LDX, 2101	0.023	0.225	21.36	1.56	0.29	0.31	-	4.91	0.66	0.029
2304	0.02	0.115	23.3	4.8	0.45	0.3	-	-	-	-
2205	0.02	0.17	22.41	5.68	3.15	0.156	0.004	1.5	0.4	-
LDX, 2404	0.025	0.245	23.98	3.65	1.63	0.36	-	2.96	0.28	-
2507	0.02	0.27	25.07	6.91	3.82	0.22	-	0.83	0.23	-

Eleven samples of duplex stainless steel (2205, 2205 (1000), 2205 (1100), LDX 2404, LDX 2404 (1000), LDX 2404 (1100), LDX 2101, LDX 2101 (1000), LDX 2101 (1100), 2507 and (2304) were used for thermal diffusivity measurements. (1000) and (1100) refer to the annealing temperature of the above mentioned samples in 10 minutes, while the other were non-heat treated samples. Heat capacity measurements were done for as received samples only.

2.2. Experimental Techniques

2.2.1. Laser Flash Technique

A Sinku-Rico laser flash unit (model TC-7000H/MELT), with a maximum sample temperature limit of 1873 K used for the present thermal diffusivity measurements. A schematic diagram of the apparatus is presented in Figure 1. The furnace heating elements, eight in number, are made of lanthanum chromate. The samples were heated under argon atmosphere at the rate of 6 K/min. the furnace temperature was measured using s-type (Pt-10%Rh/Pt) thermocouple.

In the laser flash method, top surface of a pellet shaped sample in about (2-3 mm) thickness is irradiated by a laser pulse which provides an instantaneous energy pulse. The laser energy is absorbed on the top surface of a sample and travels through the sample. The infrared detector (IR) monitors the temperature rise of the rear surface of the sample and the temperature *vs*. time profile is obtained as shown in Figure 2. The thermal diffusivity is calculated from equation (3) [5].

$$\propto = \frac{AL^2}{t_{1/2}} \qquad \ldots(3)$$

where A: constant=1.37/ $\boldsymbol{\pi}^2$, L: thickness of sample and $t_{1/2}$ is the time required for the temperature of the rear surface to reach half of its maximum temperature.

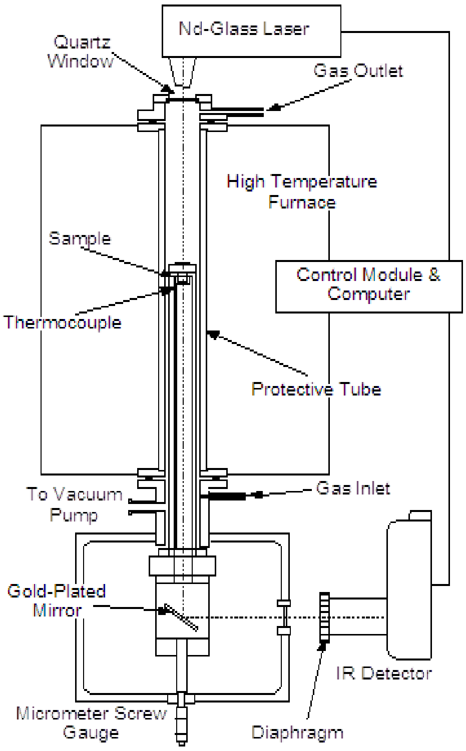


Fig. 1. Laser-Flash unit schematic diagram[5].

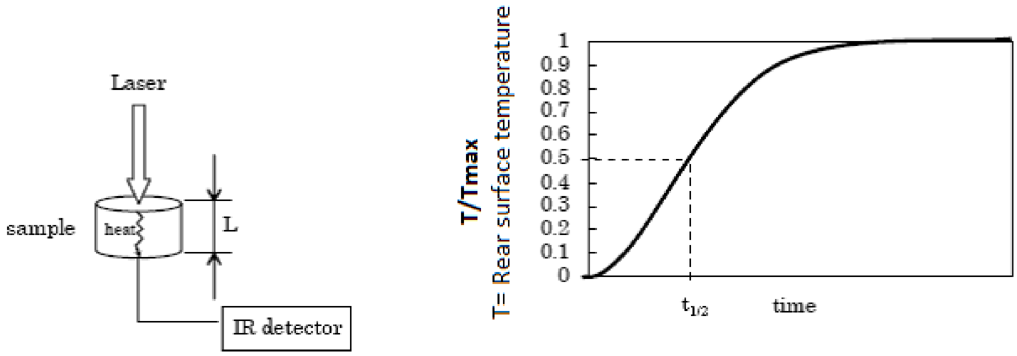


Fig. 2. A schematic illustration of sample set up and temperature *vs*. time profile of laser flash method [4].

2.2.2. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is the most frequently used thermal analysis technique alongside TGA, TMA and DMA. DSC is used to measure enthalpy changes due to changes in the physical and chemical properties of a material as a function of temperature or time. The method allows you to identify and characterize materials. An illustration of the NETZSCH STA 449C Jupiter unit used in the present work is shown in Figure 3. The apparatus was calibrated against In, Sn, Zn, Ag and Au. Fusion temperature and heats of fusion were in agreement with the literature [6]. The DSC measurements was initiated by placing the small sample of 50 milligram in weight into an alumina crucible, along with the reference with similar size specification, on the platinum sample holder provided with the previously calibrated type S (Pt-10%Rh/Pt) thermocouple . Before the experiment was started, the furnace chamber was flushed with 99, 99999% purity argon gas. The DSC measurements were conducted in the temperature range of RT -1473 K with rate of 10 K /min in heating cycle [6].

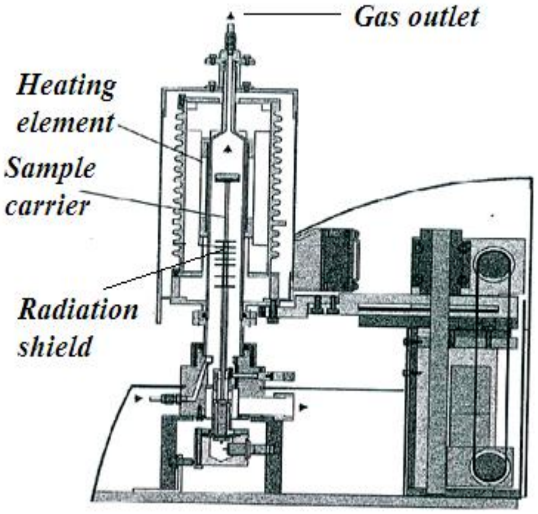


Fig. 3. Schematic of NETZSCH 449C Jupeter unit used in present work [6].

2.2.3. Scanning Electronic Microscope

Electron microscopes use electrons instead of light. In scanning electron microscopes of tungsten type as used in present work a wire of tungsten is heated to approximately 3073 K. At this temperature the electrons in the wire have such a high velocity that some of them leave the material by thermal emission. By applying electromagnetic fields these electrons can be controlled and used as an `` electron beam`` that can be directed on the sample of material that is to be investigated. Interaction between this electron beam and the sample (or specimen) results in radiation being sent out that can be detected with a suitable detector as shown in Figure 4.

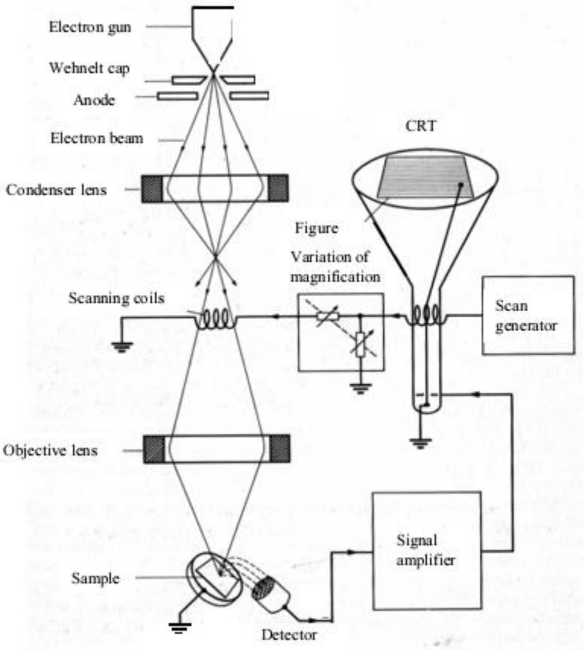


Fig. 4. A schematic diagram of an SEM [7].

2.2.3.1. The Energy Dispersion Spectroscopy Detector (EDS)

EDS is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons or a beam of X-rays, is focused into the sample being studied as shown in Figure 4 [8].

Microstructural investigations of all samples were carried out using Scanning Electron Microscopy (SEM) type (Leo 440) in resolution of light microscope 2000 Angstrom and resolution of scanning EM 50 Angstrom with wave length of electrons 0.07 Angstrom. Furthermore, Electron Dispersion Spectrometry (EDS) attached to (SEM) was used for chemical analysis of the phases.

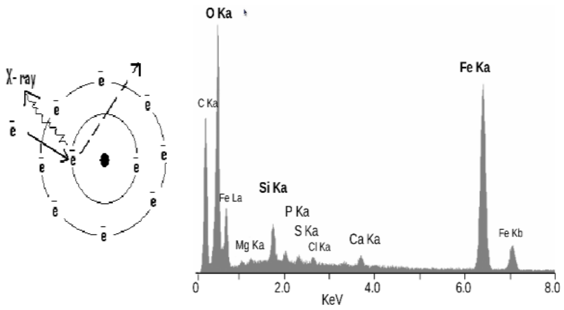
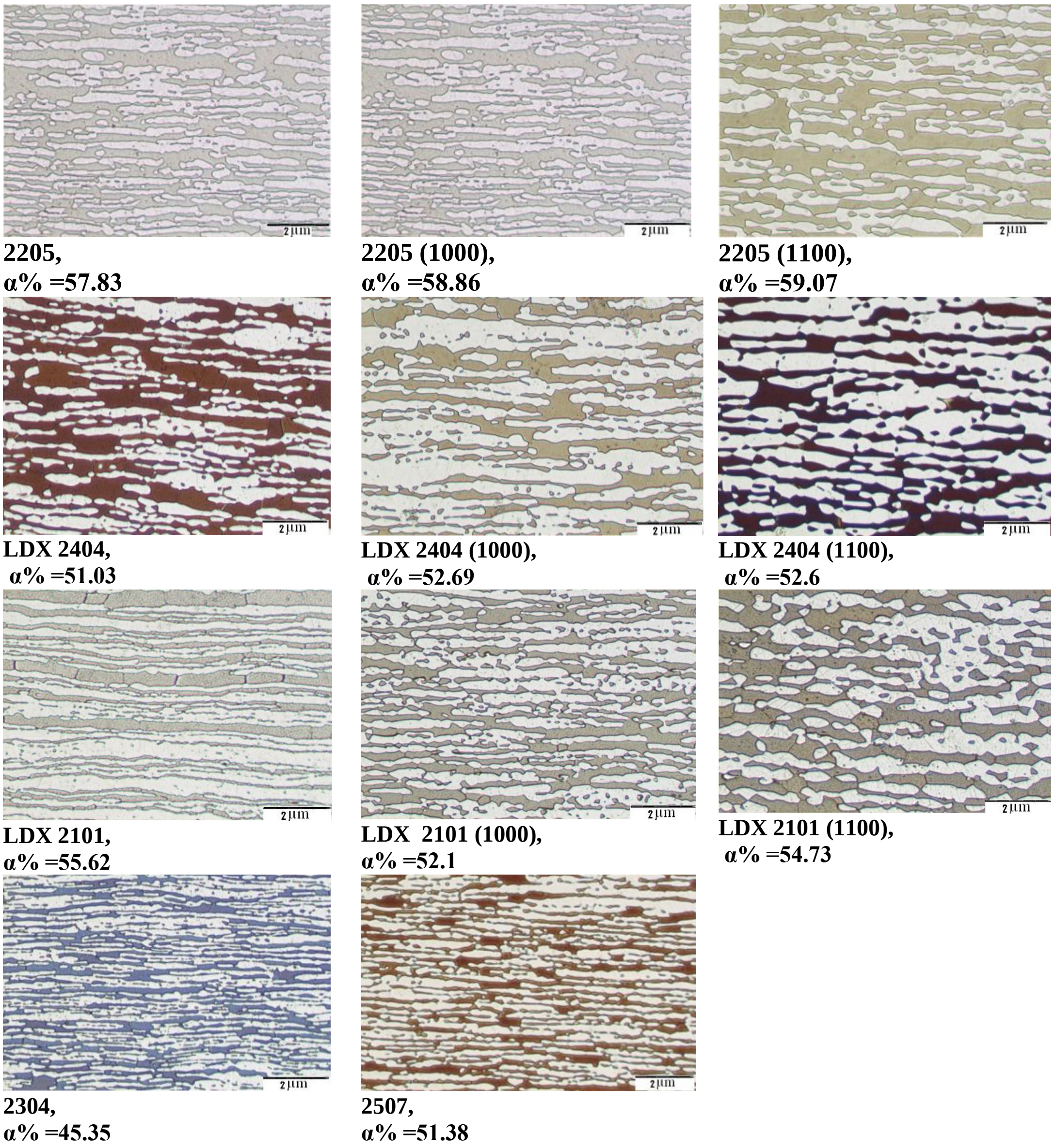


Fig. 5. Schematic of characteristic X-ray radiation [8].

3. Results

3.1 Microstructural Studies

Typical microstructures and chemical analyses of phases in duplex stainless steel are shown in Figure 6 and table 2 respectively. Austenite phase (light portion) is distributed as island in the matrix of ferrite (dark portion). It can be seen that the ferrite content increases with increasing annealing temperature of the most of the samples.



2205, α% =57.83

2205 (1000), α% =58.86

2205 (1100), α% =59.07

LDX 2404, α% =51.03

LDX 2404 (1000), α% =52.69

LDX 2404 (1100), α% =52.6

LDX 2101, α% =55.62

LDX 2101 (1000), α% =52.1

LDX 2101 (1100), α% =54.73

2304, α% =45.35

2507, α% =51.38

Fig. 6. Microstructures of duplex stainless steel. M = X 600.

Table 2,
Amount of alloying elements in the ferrite and austenite phases by using EDS attached to SEM.

Sample		Fe	N	Cr	Ni	Mo	Cu	Si
LDX 2101	α	70.89	-	22.11	1.45	-	-	0.52
	γ	71.1	-	20.7	1.78	-	-	0.45
LDX 2101 (1000)	α	71.33	0.04	24.47	1.2	0.39	0.42	0.57
	γ	72.92	0.51	21.9	1.99	0.2	0.45	0.47
LDX 2101 (1100)	α	72.91	0.21	23.77	1.25	0.43	0.42	0.56
	γ	72.68	0.58	22.18	2.01	0.29	0.46	0.53
2205	α	66.19	0.23	23.94	4.42	3.44	0.17	0.34
	γ	67.3	0.38	21.52	6.77	2.22	0.16	0.31
2205 (1000)	α	65.49	0.34	24.75	3.87	3.69	0.13	0.36
	γ	66.02	0.18	32.3	6.71	3.06	0.08	0.36
LDX 2404	α	66.14	0.08	24.09	4.48	3.3766	0.17	0.35
	γ	66.8	0.1	23.82	5.27	3.3266	0.09	0.34
LDX 2404 (1000)	α	67.58	0.11	25.58	2.99	1.87	0.44	0.35
	γ	68.12	0.63	24.01	4.03	1.14	0.51	0.27
LDX 2404 (1100)	α	66.92	0.09	26.29	2.74	2.09	0.34	0.4
	γ	67.27	0.42	24.39	4.53	1.26	0.53	0.31
2304	α	67.19	0.11	26.08	2.89	1.923	0.39	0.73
	γ	67.66	0.45	24.17	4.38	1.246	0.59	0.29
2507	α	68.4	0.03	24.92	3.93	0.406	0.30	0.60
	γ	69.36	0.43	21.8	6.14	0.31	0.44	0.55
LDX 2101	α	61.88	0.19	27.16	5.59	4.48	0.11	0.17
	γ	60.93	0.5	25.83	7.49	3.78	0.13	0.17

3.2. Thermal Diffusivity Measurements

Figure 7 shows the relation between the thermal diffusivity values and ferrite percentage of all samples at room temperature. It can be observed that is no significant effect of ferrite content in duplex stainless steel on the thermal diffusivity value at room temperature, which can be attributed to the amount of ferrite in samples are similar because the temperature of heat treatment at 1273 K and 1373 K does not show a significant changing in the phase fraction or composition of the alloys. The error bar in the thermal diffusivity measurements can be about 2-5% because of the convection effect during the measurements.

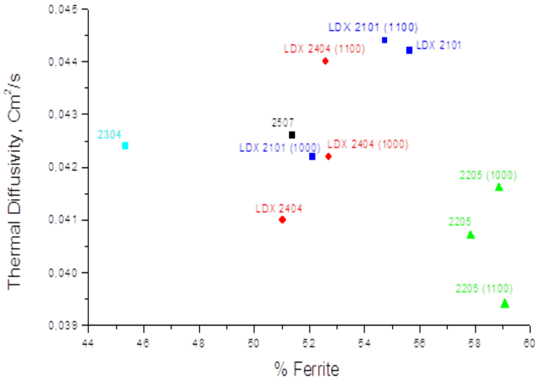


Fig . 7. Effect of ferrite content on thermal diffusivity at room temperature.

Figure 8 shows the thermal diffusivity-temperature curve for above mentioned samples. It can be seen that the thermal diffusivity increases with increasing temperature of all studied samples.

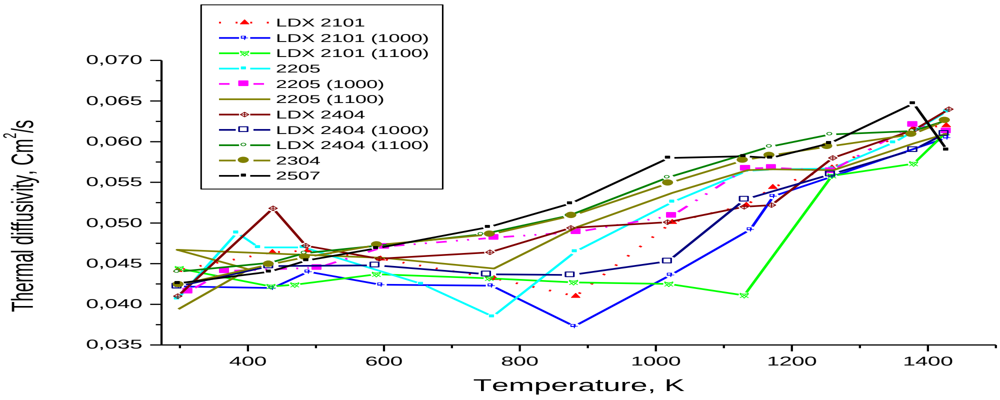


Fig . 8. Thermal diffusivity- temperature curves of the samples.

3.3. Heat Capacity Measurements

Heat capacity as a function of temperature based upon DSC measurements is presented in Figure 9 and table 3. It can be seen that the heat capacity increases with the temperature at low temperature and decreases at high temperature up to about 1100 K. Furthermore, the peak can be seen at 773 K (Curie temperature), which is the limit temperature of a ferromagnetic substance, loses its ferromagnetic properties and behaves as a paramagnetic substance. Another peak can be recognized above 1100 K, which can be due to the sigma phase precipitation. Sigma phase (σ) is one of the secondary phases that nucleate and grow after relatively long holding time during the heat treatment. The precipitation of σ phase can be represented by a eutectoid reaction ($\alpha \rightarrow \sigma + \gamma_2$) where ferrite phase is transformed into σ phase, which is enriched in Cr and Mo, and γ_2 phase (secondary austenite), which can be depleted in Cr and Mo. The nucleation of σ phase generally starts at the α/ γ boundaries and proceeds towards the ferrite phase until its complete transformation [9]. Small amount of the samples and the small changing of chemical composition of the sample surface, leads to error bar about 3 to 5% of all heat capacity values.

Table 4 summarizes the measured thermophysical properties of the duplex stainless steel samples used in the present work at room temperature.

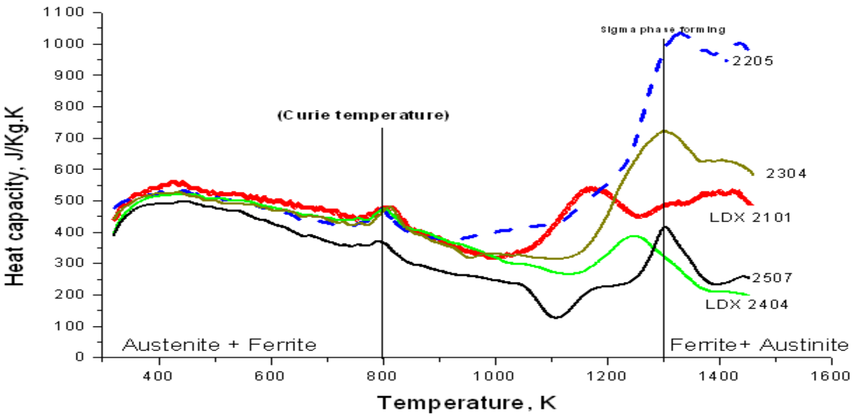


Fig. 9. Heat capacity- temperature curves of the samples.

Table 3,
Heat capacity- Temperature of the samples.

Cp, J/kg.K	373 K	473 K	573 K	673 K	773 K	873 K	973 K	1073 K	1173 K
LDX, 2101	520	530	510	480	450	390	330	360	540
2205	520	530	490	440	390	390	420	420	520
LDX, 2404	500	520	490	450	440	400	340	290	290
2304	510	510	490	450	420	390	330	320	370
2507	480	490	440	390	360	290	260	190	220

Table 4,
Thermophysical properties of the duplex stainless.

Sample	Thermal diffusivity, m^2/s	Heat capacity, J/kg.K	Density, kg/m^3	Thermal conductivity, W/m.K
LDX, 2101	$44.\ 10^{-7}$	440	7.72	14.95
2205	$41.\ 10^{-7}$	480	7.70	15.15
LDX, 2404	$41.\ 10^{-7}$	400	7.72	12.66
2304	$42.\ 10^{-7}$	440	7.75	14.32
2507	$43.\ 10^{-7}$	400	7.83	14.81

4. Discussion

Figure 10 shows the thermodynamic stabilities of the alloys under investigation at various temperatures were carried out with the help of Thermo-Calc software, which is a powerful software package for thermodynamic calculations. It is widely used for a variety of calculations including calculating stable and meta-stable heterogeneous phase equilibria, amounts of phases and their compositions, thermochemical data such as enthalpies, heat capacity and activities, transformation temperatures such as liquidus and solidus, driving force for phase transformations and phase diagrams (binary, ternary and multi-component [10,11].

Figure 6 and table 2 shows that is no significant increasing of ferrite content, when the heating temperature increased from 1273 to 1373 K. These results have a disagreement with the thermal calculation curves calculated using Termo-Calc software. It can be due to the measured values could not be reached the equilibrium state as calculated values using Thermo-Calc software.

On the other hand, it can be seen that the thermal diffusivity is nearly constant up to 773 K as shown in Figure 8. Beyond that, there was an increase of the thermal diffusivity values. In general, the increase of the slope of the curves can be due to increase in the portion of the ferrite in the structure, as shown in Figure 10 also. Furthermore, the heat capacity increases with increasing temperature at low temperature and decreases at higher temperature. The peak at about 773 K refers to Curie temperature of the samples as shown in Figure 6. At high temperature the increasing of heat capacity with temperature can be due to increase ferrite portion in the structure. Sigma phase forming can be recognized in the curves at about 1023 K for LDX 2404 and 2507 duplex stainless steel samples. If a ferromagnetic transition exists in a metal, thermal diffusivity always decreases from room temperature to the Curie temperature, as the disorder increases.

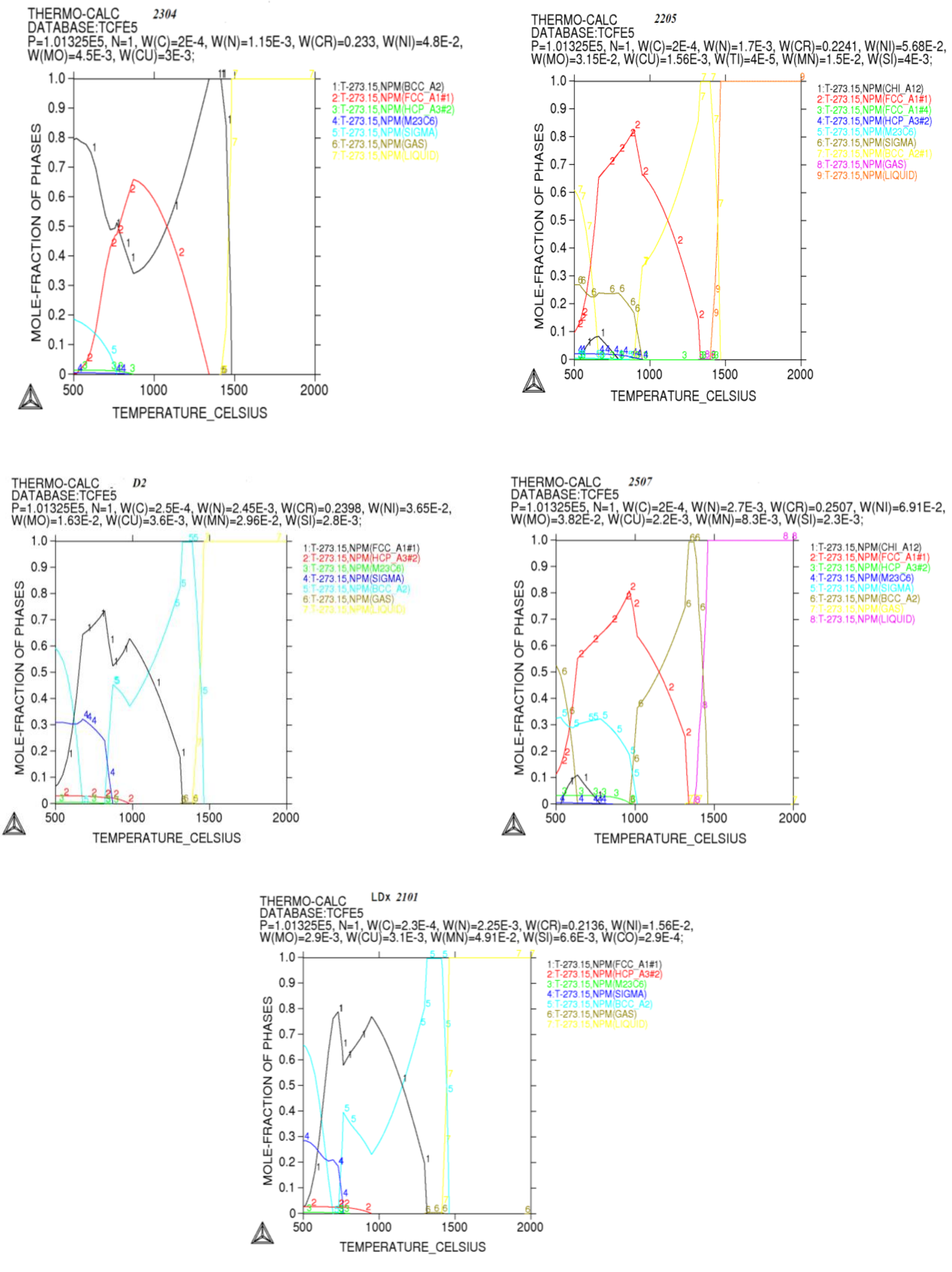


Fig. 10. Thermo-Calc results of alloys.

5. Conclusions

1. The ferrite content in the duplex stainless steel increased with temperature at equilibrium state. While in present study the equilibrium state could not be reached and there is no significant change at 1273 and 1373 K.
2. There is no significant effect of ferrite content in duplex on the thermal diffusivity value at room temperature.
3. There is no significant increasing of thermal diffusivity of the samples up to 773 K. Beyond that there is an increasing of thermal diffusivity with the temperature.
4. Heat capacity of all samples increases with temperature from room temperature to 473 K, while it decreases with increasing temperature until 1073 K. Then it increases with temperature at higher temperature.
5. Curie temperature and sigma phase formation temperature can be detected from heat capacity-temperature curves.

Acknowledgment

The authors acknowledge the support received from the Avesta Research Centre and Royal Institute of Technology, Stockholm, Sweden for carrying out the present investigation.

6. References

[1] S. Seetharaman, Du. Sichen, R. Eriksson, E. Kapilashrami, High Temperature Materials and Processes. Volume 22, Issue 5-6, pp. 283–290.

[2] R. Abdul Abas, M. Hayashi, S. Seetharaman, Thermal Diffusivity Measurements of some Industrially Important Alloys by a Laser Flash Method, Int. J. Mat. Res. (Zeitschri fur Metallkunde) 2007, vol. 98, pp. 535-540.

[3] W. D. Callester, Material Science and Engineering, chapter 17, pp.720.

[4] S.V. Stankus, I.V. Savchenko, A.V. Baginiskii, O.I. Verba, A.M. Prokop and A. Khairulin, High Temperature, 2008, Volume 46, No 5, pp. 731-733.

[5] T. Matsushita and S. Seetharaman, High Temperature Process Theory (MH2453), Division of Materials Process Science, 2009-07-01

[6] NETZSCH Instrument, Thermal analysis software, Proteus, for MS Windows, ver 4.2, Aldridge, west Midlands UK, (2003).

[7] J.Goldstein, Scanning Electron Microscope and X-Ray Microanalysis. Third Edition ed. 2003.

[8] Joseph Goldstein (2003). Scanning Electron Microscopy and X-Ray Microanalysis. Springer. ISBN 978-0-306-47292-3.

[9] E. Bettini1 et al, Int. J. Electrochem. Sci., 9 (2014) 61 – 80.

[10] J-O. Andersson, T. Helander, L. Höglund, P. Shi, B. Sundman: Elsevier Science LTD, Thermo-Calc & Dictra, computational tools for Materials Science Calphad, 26 (2002), 273.

[11] A. Rudajevova and J. Burianek, Journal of Phase Equilibria Vol. 22, No.5, 2001. pp. 560-563.

دراسة تجريبية للأنتشارية الحرارية و السعة الحرارية المتعلقة بالفولاذ المقاوم للصدأ المزدوج

رياض هرول عبد العباس*   نبيل كاظم تايه**
**مركز بحوث افيستا/ السويد*
***المعهد التقني/ كوت*
*البريد الالكتروني: Riad_riri@hotmail.com
**البريد الالكتروني:nkadom123@gmail.com

الخلاصة

تم في هذا البحث قياس الأنتشارية الحرارية و السعة الحرارية على عينات لمجموعة مختلفة من سبائك الفولاذ المقاوم للصدأ المزدوج و المجهز من شركة أوتوكومبو السويدية وتمت التجارب على هذه العينات ضمن مدى من درجات الحرارة تراوحت بين درجة حرارة الغرفة و درجة حرارة 1473 K. أن الهدف من هذه الدراسة هو الحصول على بيانات معتمدة وموثوقة لهذه السبائك من حيث خواصها الفيزيوحرارية . لقد أظهرت النتائج أن محتوى الفرايت في سبائك الفولاذ المقاوم للصدأ المزدوج يزداد مع أزدياد درجة الحرارة في حالة التوازن الحراري ، ومن ناحية أخرى أن محتوى الفرايت يزداد كذلك مع أزدياد نسبة الكروم الى النيكل وقد بينت النتائج أيضا انه ليس هناك أي تاثير واضح لمحتوى الفرايت في الفولاذ المزدوج على قيمة الأنتشارية الحر ارية عند درجة حرارة الغرفة وعلاوه على ذلك أن السعة الحرارية لجميع العينات تزداد مع زيادة د رجة الحرارة (من درجة حرارة الغرفة حتى 473 K)، و تتناقص عند أرتفاع درجة الحرارة لغاية 1073 K، وبعد ذلك تزداد مع ازدياد درجة الحرارة. كما يمكن استخدام نتائج فحوصات السعة الحرارية لتحديد در جة حرارة كيوري و درجة حرارة نشوء طور سيكما لهذا النوع من الفولاذ المقاوم للصدأ .
