DETERMINATION OF SURFACE PROPERTIES OF Fe - C - Cr MODEL ALLOYS

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Abstract

In this paper, the dependencies of density (ρ), surface tension (σ), and average wetting angles on temperature were investigated at three Fe - C - Cr model alloys where chromium content ranged from 0.92 to 4.76 wt%. All measurements were performed by sessile drop technique in a resistance furnace at temperatures from melting point up to 1600 °C. The effect of chromium, oxygen, and sulfur on the values of the abovementioned quantities was found. The temperature coefficient of surface tension $d\sigma/dT$ was positive for all liquid metal samples due to the influence of surface active elements. The surface tension and average wetting angles raised with increasing chromium content. All obtained data were statistically evaluated with a satisfactory result.

Keywords: Surface properties, Fe - C - Cr model alloys, chromium, alumina, sessile drop method

1. INTRODUCTION

Knowledge of the surface tension and other surface properties of metal melts is widely demanded in many application fields, e.g. in the continuous casting process, welding, solidification, and in many others [1,2]. Experimental determination of given quantities is very difficult, time-consuming, costly, and brings practical difficulties that make their progress more challenging. Mainly, methodological differences in experimental procedures at the determination of surface tension and the characterization of phase interface of a molten metal/solid ceramics systems via wettability are a major source of discrepancy between different laboratories and research groups [3]. Although there are theoretical (thermodynamic) and empirical models for calculation of surface tension of metal melts, but not all can be applied to multi-component systems in a broad concentration range [4,5,6]. Therefore, experimental data of these systems are highly valued.

As already indicated, the measurements of surface properties, in particular by one of the contact methods, strongly depend on the conditions of the experiments. The physical characteristics of the substrate surface (roughness, cracking, microcavities etc.) can change wetting behaviours considerably [3]. Surface contamination of metal samples which strongly influences the value of surface tension should be minimized by adjusting specimens before the experiment. The samples can be pretreated by degreasing with solvents, chemical etching, polishing, heating and drying. Nonetheless, even the pretreatment itself can change surface properties significantly, e.g. treating stainless steel foils in an oxygen plasma enrich the surface by iron and chromium oxides [7].

The surface tension is notably affected by the chemical composition of investigated samples. Surface active elements such as oxygen and sulphur, among others, are of interest of the processing of liquid steels because they occupy the surface sites, thus markedly change surface tension [6]. In contrast, chromium has only a slight effect on surface tension particularly at systems where oxygen is not present. For binary Fe - Cr systems, the surface tension decreases slightly with increasing chromium content [8]. The dependence of surface tension on chromium content (up to 1 wt% Cr) in Fe - Cr - O systems was investigated by Tret'yakova et al. They have stated, that minimum surface tension occurs when the melt is the most microheterogeneous. The presence of chromium increased the surface tension due to its ability to penetrate between the clusters which made the melt more uniform [9]. Furthermore, the chromium possesses a strong affinity to oxygen thus facilitating its adsorption. At higher concentrations (above 10 wt%), it lowers the surface tension of Fe - Cr - O systems [10]. On the basis of experimental works of the number of authors, it cannot be stated, whether the influence of chromium on the surface tension of iron-based alloys is positive or negative. It depends on the presence of other surface-active elements, especially oxygen.

This paper deals with the measurements of quantities such as surface tension, wetting angles and density at three Fe - C - Cr model alloys where chromium content ranged from 0.92 to 4.76 wt%. The dependencies of these quantities on temperature were investigated by the sessile drop method when the model alloys were in contact with the alumina substrate.

2. EXPERIMENTAL RESEARCH

2.1. Preparation of the samples

The surface properties were investigated on three model iron-based alloy samples that differed mainly in chromium content (**Table 1**).

Table 1 Chemical composition of investigated alloys before experimental trials (wt%)

Sample	Cr	C	O	S	Mn	W	Co
1	0.9242	0.3437	0.0021	0.0675	0.056	-	0.013
2	2.9700	0.3416	0.0195	0.0522	0.050	0.024	0.020
3	4.7600	0.3401	0.0015	0.0062	0.042	0.044	0.010

The other elements (Ni, Si, Ti, Mo, P, Al, Cu and Zr) were present in an amount below 0.005 wt%. The rest was represented by iron. Each sample weighed about 0.75 g and was cylindrical in shape (height 5 mm, diameter 5 mm). Prior to the experiment, the sample was mechanically polished and then purged in acetone (analytical grade).

2.2. Measurement of surface properties

The determination of the surface properties was made by the sessile drop method. The observation of (sessile) drop resting on a horizontal plate of high purity alumina (99.8 %) with dimensions (37.3 x 44.7 x 2.0 mm) was carried out in resistance furnace Clasic. Alumina plates were annealed at 1150 °C for 5 hours and then purified in acetone before the experiment. The shape of the metal drop was recorded by the camera CANON EOS 550D during heating from temperature 1450 °C to 1600 °C in the observation chamber filled with a pure argon (99.9999 %) atmosphere. The heating rate was 5 $°C \cdot min^{-1}$. The thermocouple Pt - 13%Rh/Pt was used for the measurement of the temperature.

The in-house developed software Surface Tension version 1.0 was employed for automatic evaluation of acquired photos, drop shape recognition, surface tension, density and average wetting angles calculation. This software uses the least square method for insetting the Laplace profile.

3. RESULTS AND DISCUSSION

Experimental determination of temperature dependencies of density, surface tension and average wetting angle for samples 1 - 3 was repeatedly performed for the verification of measured data.

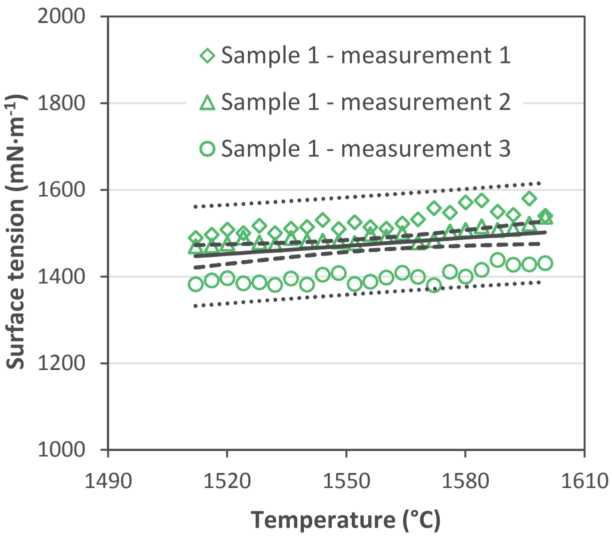

Figure 1 Temperature dependence of surface tension for sample 1

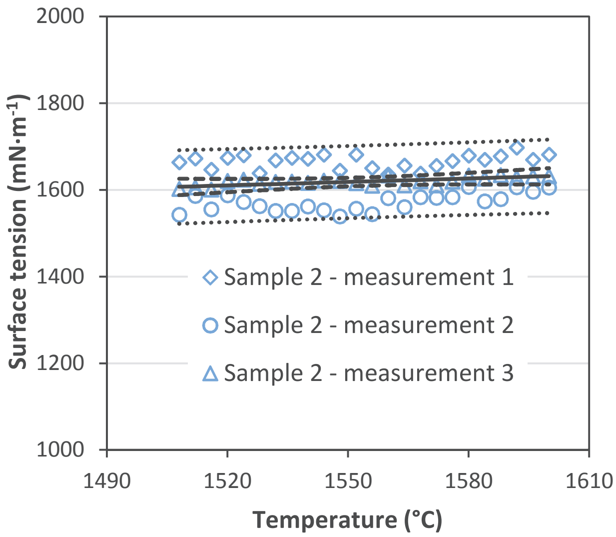

Figure 2 Temperature dependence of surface tension for sample 2

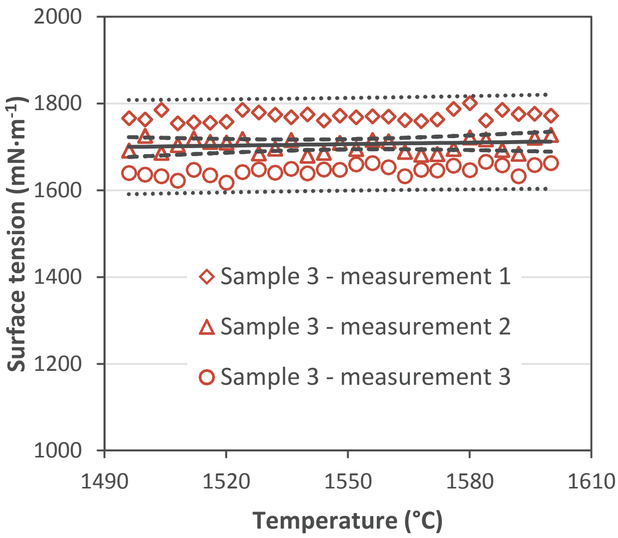

Figure 3 Temperature dependence of surface tension for sample 3

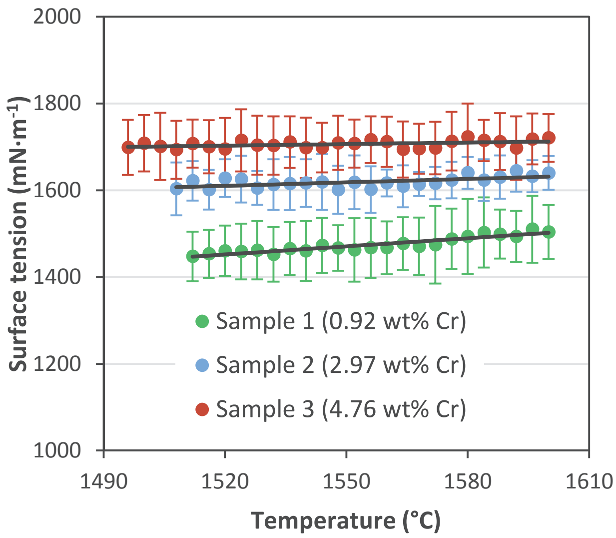

Figure 4 Dependencies of average surface tension on the temperature for samples 1-3

he statistical analysis of surface tension measurements was performed using computing environment R (R Development Core Team, 2018). **Figures 1 - 3** present the surface tension models (continuous lines), 95% confidence intervals (dashed lines), and 95% prediction intervals (dotted) lines. Only the model for the chromium content of 0.92 wt% was found to be statistically significant at a significance level 5 %. Since the surface tensions had not a normal distribution (verified using the Shapiro-Wilk test), they can be estimated by median and 95% confidence intervals (**Table 2**). Furthermore, the surface tension ranged from 1381 to 1581 mN·m^{-1} for sample 1 at temperature interval 1512 - 1600 °C, for sample 2 from 1539 to 1698 mN·m^{-1} at temperatures 1508 - 1600 °C, and for sample 3 from 1618 to 1801 mN·m^{-1} at temperatures 1496 - 1600 °C.

Figure 4 summarizes previous figures, and also present experimental scatter (coefficient of variation) of the measured data which was not greater than 5 %. As can be seen in the figure, the surface tension increases with temperature and chromium content. Therefore, the temperature coefficient of surface tension (*dσ/dT*) is positive. This is most evident in sample 1 which has the highest sulphur content (0.0675 wt%). Unlike sample 3, where the sulphur is least present (0.0062 wt%). A positive coefficient of surface tension can be explained according to [11] where, based on the Gibbs adsorption theory, the free surface of a metal droplet is covered by a monolayer of surface active elements (sulphur, oxygen) with a lower surface tension than the volume phase itself. With increasing temperature, the surface-active elements are desorbed into the bulk of the liquid metal causing a slight increase of surface tension. This phenomenon was described for samples with higher sulphur content [12].

Table 2 Statistical evaluation of surface tension dependencies on temperature (*T*)

Sample	σ = f(T); σ (mN·m^{-1}), *T* (°C)	Overall F - test (P value)	Median of surface tension + 95 % interval estimation
1	$\sigma(T)=1447+6.25\cdot10^{-1}\cdot(T-1512)$	0.016	1475 (1457; 1494)
2	$\sigma(T)=1607+2.66\cdot10^{-1}\cdot(T-1508)$	0.137	1620 (1610; 1630)
3	$\sigma(T)=1700+1.19\cdot10^{-1}\cdot(T-1496)$	0.533	1706 (1695; 1717)

The evaluation of the density is necessary for the accurate determination of the surface tension by the sessile drop method. Experimentally determined temperature dependencies of average density for all samples 1 - 3 are shown in **Figure 5**. The figure illustrates a linear drop in density with respect to temperature for all samples. Data variability expressed by the coefficient of variation was not greater than 5%. Experimental densities were compared with those theoretically calculated by means of Thermo-Calc software operating with the TCFE8 TCS8 TCS Steels / Fe-alloys Database. The database is applicable for various types of steels/Fe-alloys with the recommended content of specific alloy elements. **Figure 6** then displays the comparison of the theoretically calculated and experimentally determined densities.

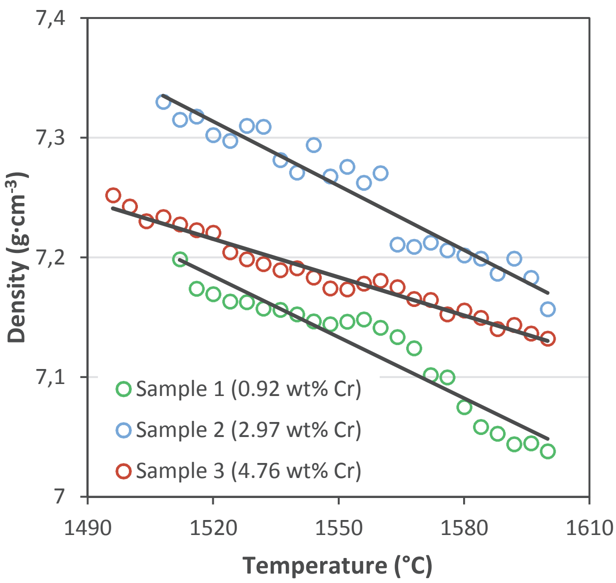

Figure 5 Dependencies of average density on the temperature for samples 1-3

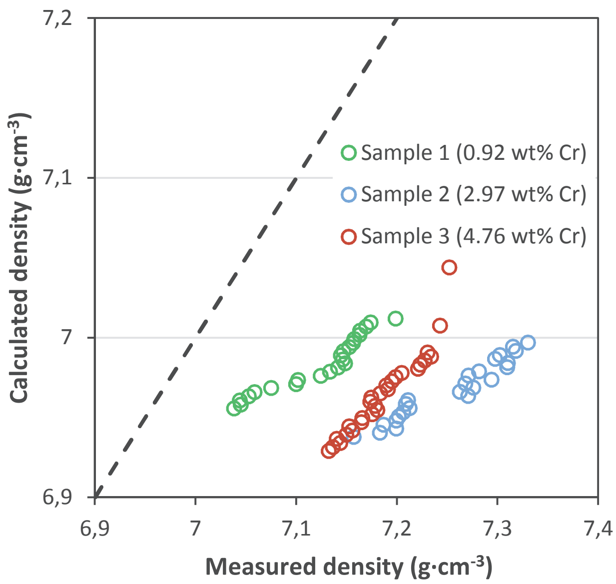

Figure 6 Comparison of experimentally obtained density values with calculated data

Figure 6 shows that the lowest difference between experimental and theoretically calculated densities is for sample 1 where the relative error at T_{min} is 2.66% and at T_{max} is 1.19%. The highest difference is for sample 2, where the relative error at T_{min} is 4.76% and at T_{max} 3.16%. The deviation of theoretical and experimental densities calculated by relative error was not greater than 5% for all analyzed samples. The linear relations of the theoretically calculated and experimentally determined densities for individual samples are shown in **Table 3** below. The differences between experimental and theoretical densities at a minimum and maximum temperatures are also presented there.

Table 3 Equations of the temperature dependence of density for experimental and theoretical data, differences ($\Delta\rho$) of experimental and theoretical densities at a maximum (T_{max}) and minimum (T_{min}) temperatures

Sample	$\Delta\rho$ ($g \cdot cm^{-3}$) at T_{min}	$\Delta\rho$ ($g \cdot cm^{-3}$) at T_{max}	ρ = f(T); ρ ($g \cdot cm^{-3}$), T (°C)	
			Experimental data	**Theoretical data**
1	0.19	0.08	$\rho(T)=9.20-1.70 \cdot 10^{-3} \cdot (T-1512)$	$\rho(T)=7.01-6.41 \cdot 10^{-4} \cdot (T-1512)$
2	0.33	0.22	$\rho(T)=7.34-1.79 \cdot 10^{-3} \cdot (T-1508)$	$\rho(T)=7.00-6.42 \cdot 10^{-4} \cdot (T-1508)$
3	0.26	0.20	$\rho(T)=7.24-1.07 \cdot 10^{-3} \cdot (T-1496)$	$\rho(T)=7.00-6.44 \cdot 10^{-4} \cdot (T-1496)$

Figure 7 shows the temperature dependencies of average wetting angle for all analyzed samples. The value of average wetting angles increased with increasing chrome content. For sample 1 with the lowest chromium content (0.92 wt% Cr), it is about 142 degrees, while for sample 3 with the highest chromium content (4.76 wt% Cr) it is about 165 degrees. Furthermore, as can be seen from the figure, the average wetting angle value increases very slightly with temperature. The coefficient of variation did not exceed 10 %.

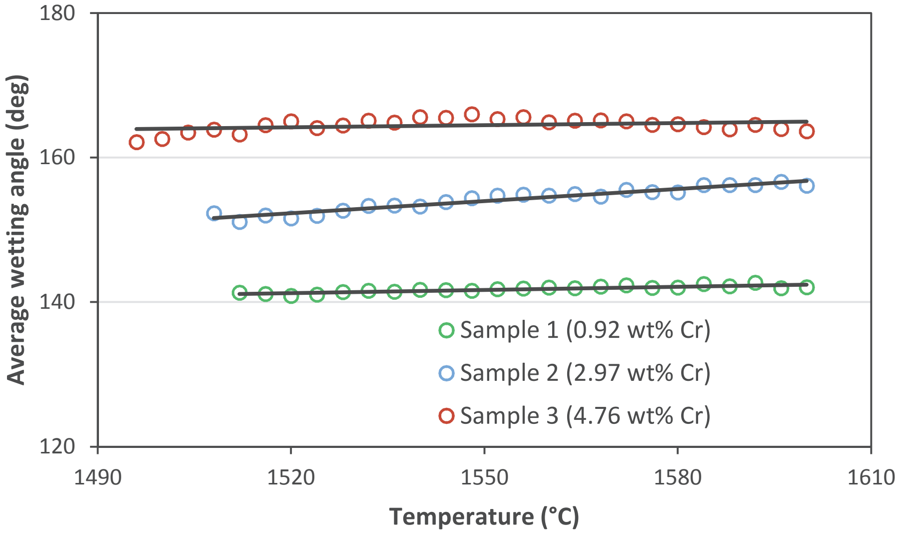

Figure 7 Dependencies of average wetting angle on the temperature for samples 1-3

4. CONCLUSION

The surface properties of three Fe - Cr - Cr alloys, which mainly differed in chromium content, were measured in the temperature range from the liquid temperature to 1600 ° C. The following results were obtained.

- The surface tension increased with a rise in temperature at all Fe - C - Cr alloys, and the temperature coefficient of surface tension ($d\sigma/dT$) always has been positive.
- The temperature coefficient of the surface tension depended on the sulphur content of the alloy samples. The maximum value was obtained for sample 1 with the highest sulphur content and the lowest for sample 3 where the sulphur content was insignificant.
- The elemental composition had an impact on the value of surface tension of the alloys examined. It raised with increasing chromium content and decreasing sulphur content.

- A negative linear relationship of experimentally determined densities on temperature was observed. The calculation of theoretical dependencies showed similar course. The maximum deviation of the theoretical and experimental densities expressed by relative error wasn't higher than 5%.
- The size of the wetting angles grew slightly with increasing temperature and positively depended on the chromium content in the analyzed samples.

Confirmation of the results mentioned above will be completed by SEM and EDX analyzes to deeper understand the influence of composition and temperature on the surface properties of Fe - C - Cr alloys.

ACKNOWLEDGEMENTS

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