EFFECT OF TEMPERATURE AND CHEMICAL COMPOSITION ON SURFACE PROPERTIES OF LIQUID ALLOYS BASED ON Fe - C - Cr

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Abstract

The presented paper is focused on the experimental study of the surface properties of selected commercial steels (three alloys based on Fe - C - Cr). The surface tension of given steels and their wetting with alumina substrate in the temperature interval from the melting point to the temperature of 1600 °C were determined using the sessile drop technique. The effect of the temperature and the chemical composition on the surface properties of the steels was studied. For an assessment of the influence of the major elements (carbon and chromium), the steels with different carbon and chromium contents, which varied in the range of 0.077 - 0.381 wt. % and 0.049 - 4.990 wt. %, respectively, were chosen. It was shown that higher content of both abovementioned components increased the surface tension of the investigated steels and their contact angle with alumina substrate. The interaction of the steel samples with the alumina substrate was studied using SEM, EDX and XRD methods.

Keywords: Sessile drop method, surface tension, wetting angle, interaction, steels

1. INTRODUCTION

The surface tension of liquid Fe - alloys and their wettability of the solid substrate belong to the physicochemical quantities of prime importance in various fields of materials science and engineering. For instance, their knowledge is needed to calculate the work of adhesion of a metal on a solid, to evaluate the capillary pressure that controls infiltration of the liquid metal into porous solids or to describe behaviour at the liquid metal/crucible interface (liquid/solid phase). Surface tension data is essential to understand various phenomena in casting, refining and welding processes such as separation of inclusions from steel to slag, nucleation of bubbles and inclusions, a growth of bubbles and inclusions, spreading of inclusions in slag and others.

It is important to note that experimental study of the surface properties of a liquid multicomponent metallic alloy using some of the contact methods is very difficult especially because of the high reactivity of metallic melts with solid substrates at high temperature, chemical heterogeneity, roughness and porosity of the substrate surface, extreme sensitivity of surface tension to impurities [1]. However high - temperature wettability of the ceramic material by the liquid steel is a very important parameter for the assessment of their mutual interaction, e.g. during the casting process. The characterization of a solid surface by determination of drop contact angles aids to understanding physicochemical processes at the interface.

Even though the influence of carbon and chromium on the surface tension of steel has been studied by many authors, the results of these studies are very different. Kawai et al. [2] showed that the carbon acts as a surface - active element, i.e. it reduces the surface tension of steels. By contrast, Morohoshi et al. [3] provided that the surface tension of the Fe - C melt is constant in carbon activity range 0.1 - 0.73. During the measurement by the oscillating drop method, the partial pressure of oxygen was less than 10^{-10} Pa to minimize its effect on the surface tension. They stated that carbon does not affect surface tension, but reduces oxygen activity in the melt, causing increased surface tension. According to Lee and Morita [4], carbon has the positive effect on the activity of sulphur which lowers surface tension. Jimbo and Cramb [5] argue that the higher carbon content causes a small increase in the surface tension of the molten iron. The influence of chromium on surface tension was investigated by Li and Mukai [6, 7]. They found that chromium slightly increases surface tension. The cause of the discrepancies among results has not yet been clarified. Some are probably due to different concentrations of oxygen and sulphur in examined samples or less precise experimental techniques. It is generally known that oxygen and sulphur are among the strongly surface - active elements and therefore reduce the surface tension of steels.

The presented work is focused on the experimental study of temperature dependencies of surface tension and wetting angles of selected commonly used steels with different carbon and chromium content. The values of mentioned quantities were determined by the sessile drop method when the molten steel was in contact with the alumina substrate. The mutual interaction between the melt and solid phase was studied by means of the SEM, EDX and XRD methods.

2. EXPERIMENTAL RESEARCH

2.1. Samples characterization

Three steel grades - alloys based on Fe - C - Cr (samples 1 - 3) were used for experimental measurement of surface properties, the chemical composition of which is shown in **Table 1**. From given steels, the cylindrical pieces (diameter 5 mm x height 5 mm) were prepared, each weighting about 0.7 g. The steel pieces were mechanically polished to remove any surface oxide and cleaned with acetone.

The high purity Al_2O_3 (99.8 %) plate (37.3 x 44.7 x 2.0 mm) was used as a substrate (a non-wettable plate) in this study. Each Al_2O_3 plate was annealed at the temperature of 1150 °C for 6 hours and its surface immediately before the experiment was cleaned with acetone, dried and used without touching the surfaces, in order to avoid any possible contamination. Then the steel sample was set on the upper surface of the Al_2O_3 substrate and prepared for the experiment.

Table 1 Chemical composition of the steels (wt. %)

Sample	C	Cr	Mn	Si	P	S	Cu	Ni	Mo	Al	N	O
1	0.077	0.049	0.635	0.201	0.021	0.008	0.064	0.027	0.003	0.026	0.004	0.002
2	0.318	1.539	0.460	0.270	0.008	0.001	0.100	0.887	0.194	0.820	0.002	0.001
3	0.381	4.990	0.380	0.940	0.008	0.001	0.090	0.264	1.160	0.025	0.0068	0.001

Contents of other elements present in given steels are the following: < 0.003 Ti, < 0.003 Nb, < 0.0005 B, the rest is iron.

2.2. Measurement of surface properties

Experimental measurement of surface properties (wetting angles, surface tension) was performed in a resistance observation furnace Clasic [8] in the temperature interval from the melting point of given steel sample to the temperature of 1600 °C by the sessile drop method. This method is based on automatic recognition of the geometric shape of a drop, which is sessile on a non-wettable plate. Recognition of the drop shape is divided into two steps. Firstly, the approximate height of the drop in the image is estimated. Secondly, the contour segments of the drop are found. The Laplace - Young equation is used for evaluation of the image. Laplace method uses the global information provided by the outline of the object being watched.

Prepared sample was settled at the centre of the furnace near the thermocouple. The reaction chamber was sealed and evacuated and then purified with argon gas (> 99.9999 %). Then the system was heated to the temperature of 1600 °C at the heating rate 5 °C / min. The temperature was measured by the thermocouple Pt - 13%Rh/Pt. The shape of the sessile drop was monitored by the camera CANON EOS 550D when the sample was melted. The images of the drop were recorded only during the heating. The experiment was performed under an inert atmosphere of argon in order to avoid the oxidation of the sample.

2.3. SEM - EDX and XRD methods

The semiquantitative X-ray microanalysis of microstructural particles was carried out by scanning electron microscope JEOL 6490LV (SEM), equipped with EDX analyser INCA in the mode of backscattered electrons (BSE). The local chemical composition was determined by detecting the characteristic X-rays generated at the point of impact of the primary electron beam on the sample using the X-ray microanalysis. The experiments were performed with settings: thermo-emission cathode LaB_6, voltage 20 kV, resolution of 3.0 nm, vacuum $2.5 \cdot 10^{-6}$ Pa for metal and 25 Pa (low vacuum) for ceramics samples.

A Quanta-650 FEG auto-emission electron microscope (Thermo Fisher Scientific/FEI) was used for the acquisition of high-resolution images (see **Figures 5 - B, C, E, F, H, I**). The measurement parameters were as follows: voltage 20 kV, current 8 - 10 nA, beam diameter 6 μm, and reduced vacuum with pressure in chamber 50 Pa. The samples were measured without metal coverage.

The X-ray powder diffraction (XRD) measurements were conducted by a Bruker-AXS D8 Advance equipped with a silicon strip LynxEye position-sensitive detector under the following conditions: radiation CuKα / Ni filter, voltage 40 kV, current 40 mA, step by step mode of 0.014° 2Θ. Total time on the step was 25 s and angular extent was 5-80° 2Θ. The data were processed by the Bruker AXS Diffrac, Bruker EVA and Bruker Topas software. PDF-2 database (International Centre for Diffraction Data) was used for phase identification. The samples were measured on untreated surfaces through their central parts.

3. RESULTS AND DISCUSSION

The temperature dependencies of the surface tension of the steel samples in the temperature interval from their melting point to the temperature of 1600 °C are shown in **Figure 1**. From this figure, it is evident that the surface tension decreases with increasing temperature.

Increasing content of carbon and chromium acts positively on the steel surface tension, this means that with increasing content of the abovementioned elements the surface tension increases, see **Figure 1**. However, the surface tension of investigated steels can be affected by the presence of surface active elements such as oxygen and sulphur, which were present in the steels already before the experiment. Therefore, it is possible to lean towards the opinions of the authors [3, 4, 9]. According to their findings, the effect of carbon and chromium is greatly influenced by the presence of surface active elements. Carbon itself does not influence the surface tension but reduces oxygen activity in the melt which causes an increase in the surface tension. Carbon may also increase the sulphur activity causing a decrease in the surface tension, whereas at the same time carbon itself increases the surface tension. The presence of oxygen also influences the effect of chromium on the surface tension. Chromium has a relatively strong affinity to oxygen. Therefore, lowering of the oxygen activity in the melt consequently increases the surface tension.

The temperature dependencies of the average wetting angle of the steel samples in the temperature interval from their melting point to the temperature of 1600 °C are shown in **Figure 2**.

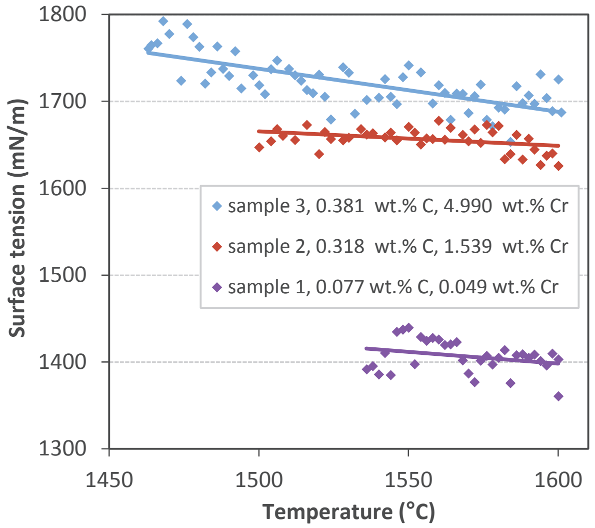

Figure 1 Temperature dependencies of the surface tension of investigated steel

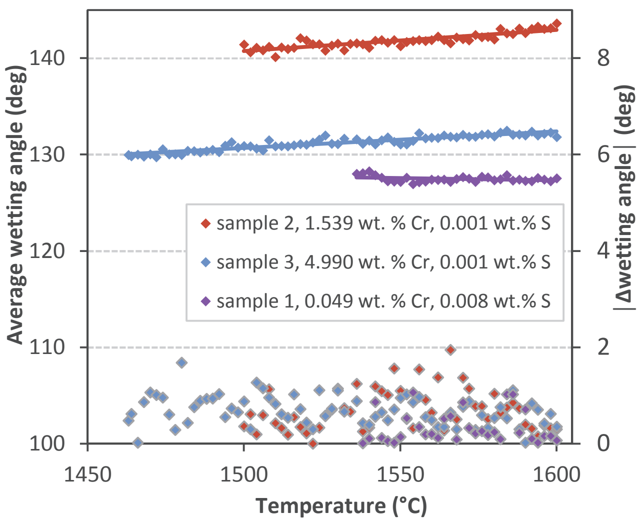

Figure 2 Temperature dependencies of average wetting angles of investigated steels on alumina substrate

The absolute value of the difference between the right and left wetting angle, which does not exceed the value of 2° for any of the samples over the entire measured temperature interval, can be found there. From **Figure 2** it is apparent that higher chromium content increases the wetting angles, except for sample 2 which possess a higher amount of aluminium (0.820 wt. %). SEM analysis indicated that Al_2O_3 was locally formed on the sphere surface at the contact with the alumina substrate, see **Figure 3** (c). It probably influenced the value of the wetting angles.

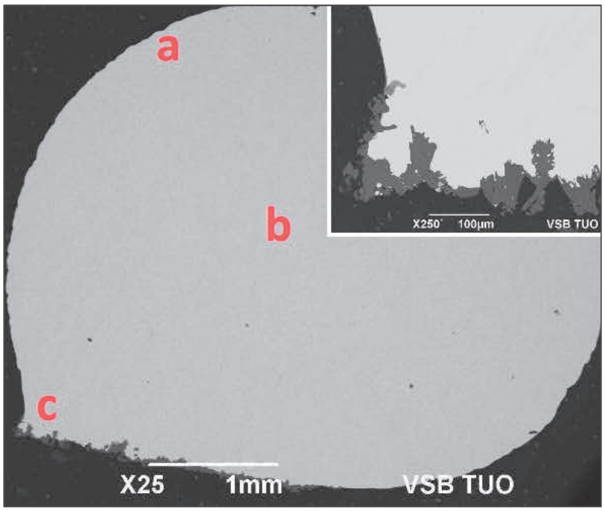

Figure 3 SEM image of the droplet, a - c) analyzed regions. The detail of the contact between droplet and alumina substrate (c)

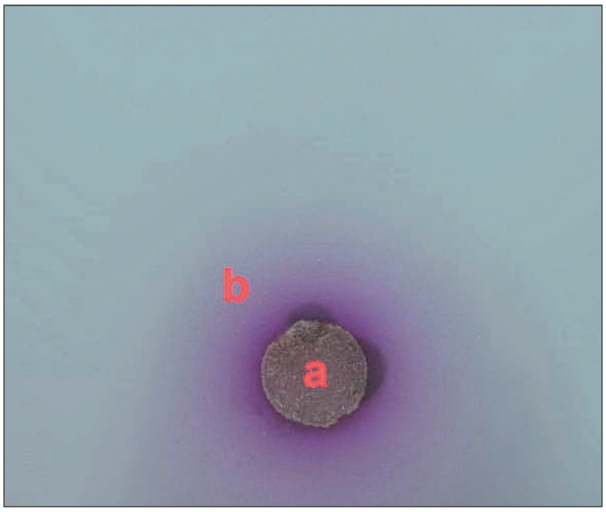

Figure 4 The surface of the alumina substrate, a) area under the liquid metal droplet, b) reddish circle in its proximity

The interaction of steel samples with the alumina substrate was investigated using SEM and EDX analysis. **Figure 3** (SEM image) shows a metal droplet (sample 2) after the experiment. Individual analyzes were performed in marked regions. EDX observation was carried out to clarify the surface distribution of selected elements. Based on EDX analysis, it can be stated that none of metal droplet samples was covered by the oxidation layer. There was also no dissolution of the aluminium in the melt. The chromium content at sample

3 slightly decreased from its original value 4.99 wt. % to 3.41 - 4.1 wt. %. All samples examined showed a moderate increase in silicon content. Specifically, for sample 1 from the beginning value 0.201 wt. % to 0.23 - 0.26 wt. %, for sample 2 from 0.270 wt. % to 0.42 - 0.55 wt. %, and for sample 3 from the original 0.940 wt. % to 1.41 - 1.72 wt. %. The alumina substrate after the experiment is shown in **Figure 4** with highlighted analyzed areas, the area under the melt droplet and the area in the immediate vicinity (reddish ring formed around it). **Figure 5** displays SEM images of the alumina substrate after the experiment. Analyzed surface area and the points of the individual analyzes are shown in **Figures 5A, 5D** and **5G**. The surface under the liquid metal droplet is in **Figures 5B, 5E, 5H**, and the area around in **Figures 5C, 5F** and **5I**. EDX analysis for sample 1 confirmed enrichment by iron (0.14 to 0.65 wt. %) in the area under metal droplet and its immediate vicinity (see **Figures 5B, C**). Calcium is present in a higher amount in the area under the melt in the range 0.79 - 2.55 wt. %. X-ray diffraction confirmed the occurrence of the high-temperature mineral hibonite (theoretically $CaAl_{12}O_{19}$) in the surface layer under the droplet (see **Figure 5B**). The amount of calcium was also increased in samples 2 and 3 in the same area (sample 2 (1.75 - 5.47 wt.%), sample 3 (0.62 - 8.42 wt.%)). The hibonite was present there in both samples (see **Figures 5E, H**). In the case of the two last-mentioned samples, chromium was found in the surface layer close to the droplet, probably in trivalent Cr(III) form. It is to be assumed that aluminium can be substituted for the chromium in corundum due to the similar atomic radius and is present there as chromium oxide. Furthermore, Cr(III) ion possess two strong adsorption bands in the visible part of the spectrum which explains the red color [10].

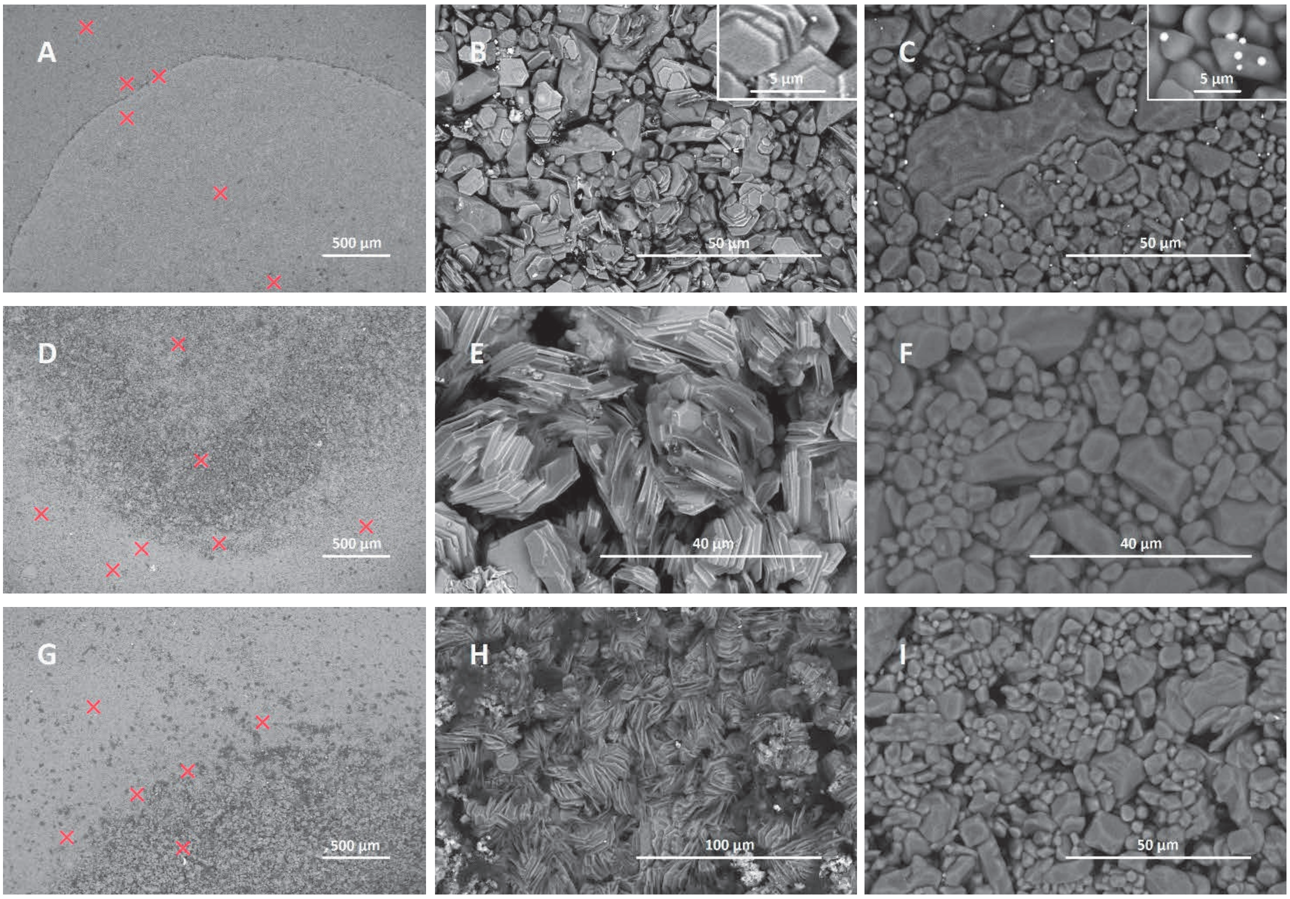

Figure 5 SEM images of the alumina substrate after the experiment for sample 1 (A - C), sample 2 (D - F) and sample 3 (G - I). SEM image of the alumina substrate after the experiment at low magnification (40x), the area under droplet, and the area in its vicinity are in the row from left to right. High - magnified (12 000x) image of sample 1, Figure (B, C) (inlay)

4. CONCLUSION

The results obtained by the experimental research can be summarized as follows:

- The surface tension of the investigated steel samples decreases with increasing temperature.
- The surface tension increases with increasing contents of carbon and chromium for all investigated steels. The positive effect of carbon and chromium on the surface tension of given steels is probably influenced by the presence of surface active elements - oxygen and sulphur. Carbon and chromium decrease the oxygen activity and consequently increases surface tension.
- The contact angle of liquid steel samples with alumina substrate increases with increasing chromium content. Wetting angle decreases markedly with the increasing content of sulphur. The wettability of alumina at investigated steels increases slightly with increasing temperature.
- The interaction of the melt with the alumina substrate can be affirmed from the results of SEM, EDX, and X-ray diffraction analysis. Nevertheless, there was no formation of oxidation layer on the surface of the metal droplet and aluminium dissolution in the melt. The hibonite was formed in the alumina substrate at the point under the metal droplet for all three analyzed samples. It was enriched with iron in the case of sample 1, which had the lowest chromium content (0.049 wt. %). Furthermore, it was found that isomorphic substitution of Cr^{3+} for Al^{3+} occurs in the corundum surface layer near the metal droplet at samples 2 (1.539 wt. % Cr) and 3 (4.990 wt. % Cr). The chromium was present there as Cr_2O_3.

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