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## THE ANALYSIS OF CHANGES IN FORCES CAUSED BY SOLID PROBE PASSAGE THROUGH INTERFACE BETWEEN TWO FLUID PHASES

A significant role in metallurgical and foundry processes, inclusive of the ones related to composite material technology, is played by interfacial tension arising in technological systems. In the systems related to the technology of composite castings (both ones reinforced with particles and with saturated reinforcement), interfacial tension, particularly during recycling processes, appears at the boundaries of three phases: liquid metal (alloy), liquid slag, and atmosphere, in any combinations. Knowledge of the values of these parameters facilitates the designing of technological processes. Therefore, a useful measurement method of these tensions should allow for the measurements to be carried out during a single experiment. The authors have tested a chosen method, being a combination of plate and ring methods, and found its usefulness in the case of systems composed of liquid aluminum alloys and melted salt mixtures. Since the method is based on the measurement and recording of the forces acting at the probe (solid phase) moving successively through a layer of liquid metal (alloy) to the layer of liquid slag and, afterwards, to the atmosphere, proper interpretation of the plots of the changes in the forces recorded by the measurement system have become very important. Observation of the measurement process in real systems is very difficult (or even impossible). Hence, the authors have carried out tests with the use of equivalent media at room temperature, and obtained model plots of the recorded changes in the force values in conditions of fully clear behaviour of the examined systems. Thanks to these experiments and the observations, the authors have attained necessary and unquestionable information for full interpretation of plots illustrating the changes of recorded forces under the conditions of tests using metallurgical systems occurring in the technology of e.g. recycling of cast composite materials in the matrix of aluminum alloys.

**Keywords:** interfacial tension, methods, measurement

## ANALIZA ZMIAN WARTOŚCI SIŁ ZWIĄZANYCH Z PRZEJŚCIEM STAŁEGO PRÓBNIKA PRZEZ GRANICE FAZ PŁYNNYCH

Znaczącą rolę w procesach metalurgicznych i odlewniczych, w tym także związanych z technologią odlewanych materiałów kompozytowych, odgrywają napięcia międzyfazowe obecne w układach technologicznych. W układach związanych z technologią odlewów kompozytowych (zarówno zbrojonych cząstkami, jak i z nasycanym zbrojeniem), a szczególnie w procesach recyklingu, napięcia międzyfazowe występują na granicach trzech faz: ciekłego metalu (stopu), ciekłego żużla i atmosfery, w dowolnych kombinacjach. Znajomość wartości tych parametrów ułatwia projektowanie procesów technologicznych. Z tego powodu, przydatna metoda pomiarowa tych napięć winna umożliwić dokonywanie pomiarów w trakcie jednego doświadczenia. Autorzy przetestowali wybraną metodę będącą kombinacją metody płytkowej i pierścieniowej, stwierdzając jej przydatność dla układów złożonych z ciekłych stopów aluminium i roztopionych mieszanin soli. Ponieważ metoda opiera się na pomiarze i rejestracji wartości sił działających na próbnik (faza stała), przemieszczający się kolejno przez warstwę ciekłego metalu (stopu) do warstwy ciekłego żużla, a następnie do atmosfery, istotnego znaczenia nabrała właściwa interpretacja wykresów zmian wartości sił rejestrowanych przez zastosowany układ pomiarowy. Realne układy są trudne (lub niemożliwe) do bezpośredniej obserwacji przebiegu pomiaru, wobec czego autorzy wykonali próby z użyciem mediów zastępczych i w temperaturze pokojowej, uzyskując modelowe wykresy zarejestrowanych zmian wartości sił w warunkach pełnej przejrzystości zachowania się badanych układów. Dzięki wykonanym doświadczeniom i obserwacjom uzyskali niezbędne i niebudzące wątpliwości informacje dla pełnej interpretacji wykresów zmian wartości sił rejestrowanych w warunkach prób z użyciem układów metalurgicznych obecnych w technologii np. recyklingu odlewanych materiałów kompozytowych na osnowie stopów aluminium.

**Słowa kluczowe:** napięcia międzyfazowe, metodyka, pomiary

## INTRODUCTION

Multiphase systems appear in many processes undergoing, among others, in metallurgy and foundry. They are analyzed in problems related to the technology of cast metal composite materials [1-3] and, particu-

larly, in the cases of recycling of these materials [4-7]. The interrelations between particular phases of the systems are prerequisites for the course and efficiency of the process and, moreover, their determination often

makes a basis for measurement methods of some properties of particular phases, e.g. interfacial tensions arising at the interfaces between liquid phases [8, 9]. Among important parameters characterizing the course of metallurgical processes and related to the technology of cast metal composite materials, there are the interfacial tensions at the boundaries between liquid metal - atmosphere, liquid slag - atmosphere, liquid metal - liquid slag [7, 10]. The difficulty in assessing the above mentioned interfacial tensions consists in the high temperature of the considered phases, their reactivity, and the fact that their direct observation is very limited or even impossible.

The ways of measuring the surface tension of liquid metals and alloys [11] differ each from other by their methodology, necessary equipment, time consumption, accuracy of the results, etc. In case of the need to assess the interfacial tensions in multiphase systems (e.g. liquid metal - liquid slag - atmosphere) a universal method would be required, that might consist in achieving two results in a short time interval, within the duration of a single test.

Preliminary attempts at using a combined plate and ring method [8] for assessing the interfacial tensions in the systems liquid aluminum alloy - liquid slag - atmosphere gave encouraging results [12]. Nevertheless, in these assays there were plots (changes in recorded forces) whose explicit interpretation was difficult. This was conducive to the need for the analysis referred to in the title of the present paper, that, as being performed with transparent equivalent media, enabled direct observation of the measurement course and facilitated interpretation of the results obtained with the use of real media.

## STAND AND MEDIA USED IN STUDIES

Assessment of the interfacial tension values with plate and ring methods [8] converts itself to recording the forces acting on the probe (solid phase) when it passes through the interfaces (two liquids inactive one with respect to the other, and atmosphere). In order to record the variation of the forces acting on the probe, the measurement system shown in Figure 1 [12] was used.

The probe was made of copper pipe of an outer diameter  $\Phi_{zew} = 57$  mm and wall thickness 1.4 mm. The height of the probe (the pipe segment) amounted to 10 mm. The probe was suspended with a rigid pull rod to a dynamometer of FH2 type from SAUTER, provided with standard software AFH01 (delivered by the Company). The operating range of the dynamometer amounted to  $0 \div 2$  N, with a minimal force equal to 0.001 N.

The dynamometer was fixed to a movable cross-bar of the testing machine, INSTRUM 4481, allowing for vertical motion of the probe with adjusted and controlled speed. After preliminary tests, a constant speed

of probe motion (with respect to the liquid level) was determined and adjusted to 20 mm/min. The liquids were water and oleic acid ( $\rho_{20^\circ} = 0.899 \div 0.895$ , according to manufacturer's data). The liquid system was located in a glass beaker of a 1 dcm<sup>3</sup> volume on the test machine console.

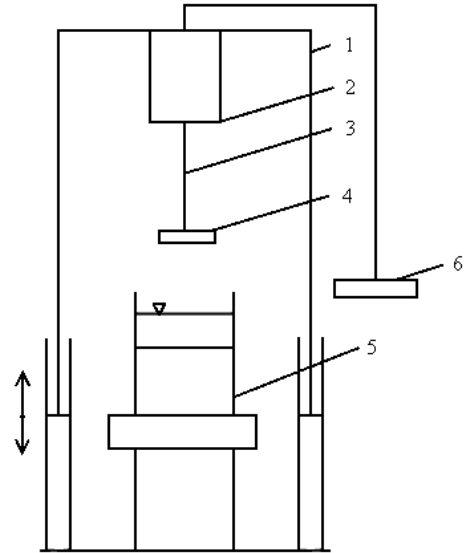


Fig. 1. Measurement system used in tests: 1 - cross-bar of the testing machine, 2 - dynamometer, 3 - rigid pull-rod, 4 - probe, 5 - vessel with liquid media, 6 - computer [12]

Rys. 1. Układ pomiarowy do wykonywania badań: 1 - trawersa maszyny wytrzymałościowej, 2 - siłomierz, 3 - sztywne cięgło, 4 - próbnik, 5 - naczynie z ciekłymi mediami, 6 - komputer [12]

## COURSE AND RESULTS OF TESTS

Two experimental series were carried out. During the first one, once the probe was fully immersed in water, the testing machine drive was put into motion and the probe emerged from the water with a constant rate and put into the oleic acid, and, afterwards, from the oleic acid to the atmosphere. Such a procedure was identical to the one used in the assays aimed at determining the values of interfacial tension: liquid 1 - liquid 2 and liquid 2 - atmosphere.

The tests of the second series were aimed at determining the changes in the forces in the time of occurrence of adhesive contact of the solid phase (the probe) with the interfaces of both liquids, and checking the symmetricity of the dynamometer indications during particular stages of probe immersion and emerging in the examined system. For this purpose the dynamometer was reset before probe immersion in oleic acid and, afterwards, the force changes were recorded on the probe path from its suspension in the atmosphere, by immersion in oleic acid and later in water. Once the drive was stopped and, afterwards, restarted, the force changes were recorded on the water - oleic acid - atmosphere path. The plots of the recorded force changes obtained in particular series were nearly identical. Therefore, the number of assays for each of the series

was reduced to three. They are shown in Figures 2 and 3.

The changes in the force recorded while the probe was emerging from water through oleic acid to the atmosphere (air) are presented in Figure 2. Once the probe was totally immersed in water the measurement-recording systems were reset.

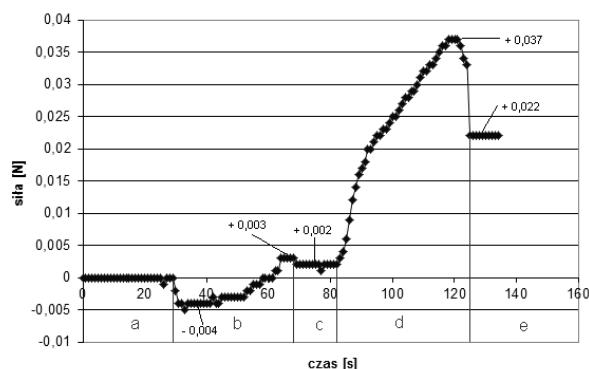


Fig. 2. Changes in force during probe emersion from water through oleic acid to atmosphere

Rys. 2. Zmiany wartości sił podczas próby wynurzania próbника z wody poprzez kwas oleinowy do atmosfery

Cycles a-e marked in Figure 2 on the time-axis are for, respectively: a - cycle of probe - water full contact, b - cycle of probe passage from water to oleic acid, c - cycle of full and exclusive contact probe - oleic acid, d - cycle of probe passage from oleic acid to atmosphere, e - cycle of total probe emergence from oleic acid and its suspension in atmosphere (air).

In the equilibrium state, the values of the recorded forces are constant. Zero force corresponds (according to the assumption) to full probe immersion in water (a). In the state of full probe immersion in oleic acid, a force growth equal to 0.002 N was found, while in full suspension in air, the growth amounts to 0.022 N.

Interesting changes in the forces are found in intermediate cycles, i.e. (b) and (d).

While the probe was emerging from water a sudden drop in the force is visible in the time of contact of the upper probe edge with the water - oleic acid interface. It amounts to 0.004 N. It is caused by two simultaneously occurring factors - the appearance of adhesion force at the contact surface of the solid (upper) phase i.e. the front surface of the copper probe with oleic acid, and the better wettability of this solid phase surface by oleic acid in a water environment than by water in an oleic acid environment, measured by the values of corresponding wetting angles. The growth of the force occurs slowly and gradually, which is due to the drop in buoyancy of the probe emerging from water. The end of the (b) cycle corresponds to the initiation of connection (contact) of the bottom probe edge with the water-oleic acid interface. A minor growth in the force value (+0.003 N) is then observable, which is caused by interfacial tension at the water-oleic acid boundary. The tension value is low, since interruption of the contact

between the bottom probe edge and the interface surface results in quite a small drop in the recorded force (to +0.002 N). The value of interfacial tension (water-oleic acid) corresponding to this difference amounts about to 3 mN/m. The beginning of the probe emerging from the oleic acid is equivalent to the start of cycle (d). Quick growth of the recorded force is initially caused by the decreasing value of buoyancy and, afterwards, to the occurrence of an oleic acid film drawn by the probe upper edge to the atmosphere. The maximum value of the recorded force reaches 0.037 N. The break of the film corresponds to a sudden drop in the force down to the level of 0.022 N. The difference between these values (0.015 N) is a measure of the interfacial tension of the oleic acid in the air atmosphere. In the condition of the present experiments it amounts to 42 mN/m.

In the second series of tests, changes in the force values were recorded during probe passage from the atmosphere through the oleic acid layer to water and in the opposite direction. The dynamometer indications were reset before each of the test trials. Similar to the first series, the plots obtained this time were almost identical. One of them is shown in Figure 3.

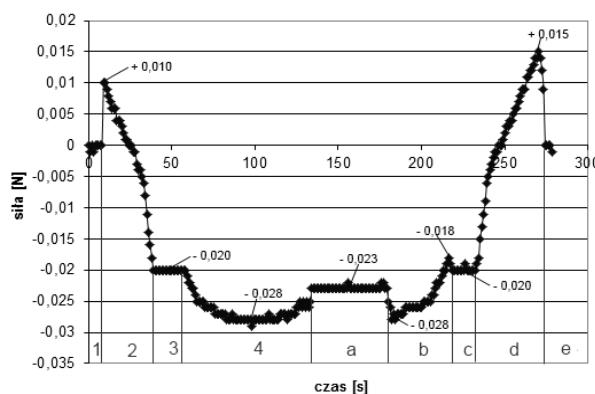


Fig. 3. Changes in force value during test of probe immersion from atmosphere to oleic acid and water, and during its emersion in opposite direction

Rys. 3. Zmiany wartości sił podczas próby zanurzenia próbника z atmosfery do kwasu oleinowego i wody oraz wynurzania w kierunku odwrotnym

Similar to the case of the description of the changes in the forces recorded during the first series of tests, the change cycles that are presented in Figure 3 may be distinguished. The particular cycles are marked with digits and letters, maintaining the same letter markings for the phenomena observed in both test series. Therefore: a - cycle of probe suspension in atmosphere above liquid level (resetting dynamometer indication) cycle of contact of probe with oleic acid and its gradual immersion cycle of total and full probe contact with oleic acid cycle of contact of bottom edge of probe with oleic acid-water interface, and its gradual immersion in water cycle of full probe contact with water cycle of probe passage from water to oleic acid (upwards) cycle of total and exclusive (full) probe contact with oleic acid cycle of probe passage from oleic acid to atmosphere

cycle of full probe emergence from oleic acid and its suspension in atmosphere.

The contact of the bottom edge of the probe (i.e. probe suspended in atmosphere) with the oleic acid surface is accompanied by a sudden growth in the force value (+0.010 N) caused by good wetting of the probe material by the acid in air atmosphere, and the occurrence of an “adhesion force” at the interface (bottom probe edge-oleic acid). Gradual immersion of the probe in oleic acid results in a drop in the value of recorded force, due to the growing buoyancy (cycle 2). Once the probe is fully immersed in oleic acid, the recorded force stabilizes (cycle 3). Since the time of contact of the bottom probe edge with the oleic acid-water interface, the force decreases due to two factors-namely the probe buoyancy and the worse wettability of the probe material by water in the oleic acid environment than by oleic acid in the water environment. The value of the recorded force reaches a minimum (-0.028 N) and then grows. The time of full probe immersion in water with simultaneous slight abrupt growth in the force value to -0.023 N ends cycle 4, after which total and full contact between the probe and water (cycle a) occurs. The change in the direction of probe motion with respect to the levels of interfaces (water-oleic acid-atmosphere) causes further course of the plot, divided into cycles (a)-(e), to comply with the description related to Figure 2.

Consideration of the plots presented in Figures 2 and 3 shows a need for detailed analysis of selected parts of both plots, particularly the ones including clear changes in the values of the recorded forces.

**DISCUSSION OF RESULTS OF STUDY**

In the ring method of measuring the values of interfacial tension in the liquid, the essence of the measurement consists in recording the maximum difference in the force recorded in the time preceding liquid film detachment from the probe surface and immediately after the detachment. Hence, in order to make a single assay, one should take the characteristics of the changes in the force values in cycles (a)-(e) of both tests. In the plots shown in Figures 2 and 3, these differences correspond to the border lines of cycles (b) and (c) as well (d) and (e). The values of interfacial tension found in both tests (Figs 2 and 3) amounted to:

- water - oleic acid: 3 and 6 mN/m
- oleic acid - air: 42 and 42 mN/m
- which were considered as satisfactory.

For cognitive purposes, the reasons for the changes in the recorded forces in cycles (1), (4), and (b) were analyzed.

Figure 4 presents a scheme of the consideration, with assumption of:

1. rectangular cross section of the probe (a segment of copper pipe)
2. three fluid media (air, oleic acid, water)

3. two directions of probe motion in the system of fluid media (immersion, emergence)

Denotation assumed for calculation purposes:

- N, G, W – force recorded by dynamometer, force of gravitation, and buoyancy, respectively
- σ (with indexes) – interfacial tension values, according to respective phases (s - solid phase, p - air, k - oleic acid, w - water)
- Θ (with indexes) – wetting angles of solid phase by liquids in various environments (air, another liquid)

Only selected conditions were analyzed, omitting the obvious ones.

The first interesting part of the experiments is the change of the research system from stage 1 to 2 (Fig. 4). It corresponds to the boundary between cycles 1 and 2 in Figure 3.

In the time of contact between the bottom probe edge with the liquid (i.e. oleic acid), vectors of interfacial tension  $\sigma_{S-K}$ ,  $\sigma_{S-P}$ ,  $\sigma_{K-P}$  appear at the edge. The result of these vectors affects the force value recorded by the dynamometer. The value of the force (Fig. 4) is equal to:

$$N_2 = G + a \left( \sigma_{S-K} - \sigma_{S-P} + \sigma_{K-P} \cos \Theta_{\frac{S-K}{P}} \right)$$

where  $a$  is the perimeter of wetted probe surface.

Knowing the geometric dimensions of the probe and the value of surface tension  $\sigma_{k-p}$  and assuming perfect wettability of the probe material by the liquid (oleic acid) in air atmosphere -  $\Theta \rightarrow 0$ , one is able, based on the difference in forces  $N_2 - N_1$ , to calculate the value of the difference in interfacial tension at the boundary between the solid phase and atmosphere:

$$\sigma_{S-K} - \sigma_{S-P} = \frac{\Delta N}{a} - \sigma_{K-P}$$

The relationship between adhesion work and adhesion force remains undetermined.

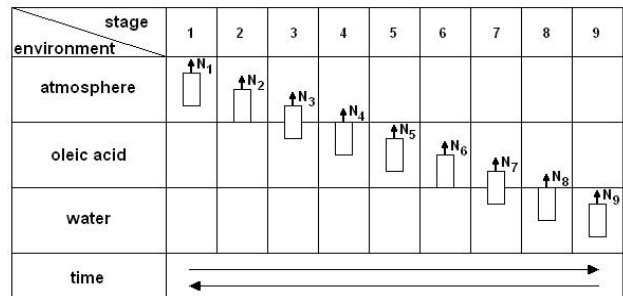


Fig. 4. Scheme depicting analysis of changes in force values recorded by dynamometer

Rys. 4. Schemat do analizy zmian wartości sił rejestrowanych przez siłomierz

Full probe immersion in oleic acid begins the cycle starting from contact of the bottom probe edge with the

interface between the oleic acid and water, which ends with full probe immersion in water. In Figure 3, this cycle is denoted by 4, while in Figure 4 it corresponds to stages 5–9.

The first contact is not accompanied by a sudden change in the value of recorded force. The change, i.e. the force drop, arises slowly. The drop from  $-0.020$  N to  $-0.028$  N is a consequence of the decidedly weak wettability of the probe material by water in the oleic acid environment, which results in pushing the probe out of the interface meniscus. Moreover, the probe buoyancy increases. Sudden changes (drops) in the force values also suggest sudden changes in the level of interface meniscus with respect to the probe. Stabilization of the recorded force ( $-0.028$  N) is equivalent to full probe immersion in water, with its contact with water occurring only on the bottom edge and vertical walls. The upper edge contacts the oleic acid but, as the probe lowers, the water-oleic acid meniscus curvature changes until the discontinuity point, i.e. until the passage of the corner edge (Fig. 5). Then the film between the oleic acid and the probe breaks and the probe is fully suspended in water. The time of the break is accompanied by a slight force growth ( $0.002$  N) and, afterwards, the force stabilizes at the level of  $-0.023$  N. The length (height) of the oleic acid film in water that is pulled by the upper probe edge may be estimated based on the time between full probe immersion (i.e. bottom and side probe wetting) and full probe contact with water ( $\sim 19$  s). It allows one to estimate the value to about  $7$  mm.

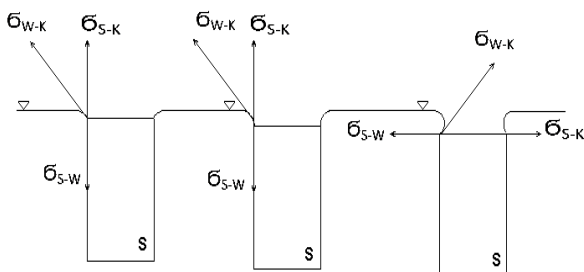


Fig. 5. Stages of shaping of interface between water and oleic acid

Rys. 5. Etapy kształtowania się powierzchni międzyfazowej woda-kwas oleinowy

The change in the direction of motion of the probe (immersed in water) begins the process of its emersion. Its first stage is denoted in Figures 2 and 3 by cycle (b). The time of contact of the probe upper edge with the interface between water and oleic acid is accompanied by a sudden drop in the recorded forces, which amount to  $0.004$  N (Fig. 2) and  $0.005$  N (Fig. 3). Gradual emersion of the probe from water is accompanied by growth of the recorded forces due to the drop in buoyancy. At the end of cycle (b), the recorded pattern of the forces indicates the occurrence of a small water film in the oleic acid environment. Break of the film is accompanied by a slight force drop (to  $0.001$  N in Fig. 2 and  $0.002$  N in Fig. 3). The difference is a measure of the

interfacial tension (water- oleic acid), which for the tests depicted in Figures 2 and 3 amounts to  $3$  mN/m and  $6$  mN/m, respectively. These values are insignificant and, moreover, they approximate the resolution limit of the measuring system. In cycle (b), the difference between the forces recorded in the time of contact of the upper probe edge and oleic acid surface (beginning of the cycle) and in the moment of break of contact between the bottom probe edge and water surface (end of the cycle) should be noticed. The drops in the force values amount to  $0.004$  N and  $0.005$  N, respectively. The difference is clear, but a question arises whether it may be a result of adhesion work performed by the system at the beginning of the cycle. Cycles (c) on both plots are equivalent to full immersion and full wetting of the probe in oleic acid. In cycles (d) the probe begins to emerge into the atmosphere (air). The growth of the force values is an effect of the drop in probe buoyancy. In both presented cases, the end of the cycle is accompanied by a remarkable increase in the values of the recorded forces, caused by the oleic acid film pulled up from the system by the bottom probe edge. Once the film breaks, the values of the recorded forces stabilize. As was mentioned before, the difference in the recorded forces is a measure of the interfacial tension between the oleic acid and air. In both cases (Figs. 2 and 3) it amounts to  $0.015$  N, that, taking into account the probe dimensions, gives a value of interfacial tension equal to  $42$  mN/m.

Let us note the difference in the values of the forces recorded in the moments of occurrence and decay of probe contact with the oleic acid surface shown in Figure 3 ( $0.010$  N and  $0.015$  N, respectively). A question arises again whether it may be a consequence of the adhesion force arising in the system.

## CONCLUSIONS

The results of the research enable formulation of the following conclusions:

- The method tested here of assessment and recording of the changes in the forces accompanying passage of the probe (solid phase) through interface boundaries (liquid - liquid and liquid - gas) appeared to be efficient and reliable.
- The observations carried out during the tests made with the use of transparent media enabled detailed interpretation of the plots showing changes in the force values recorded during the motion of a solid phase through the interfaces of the fluids. In consequence, similar plots may be a source of information related to the surface phenomena occurring at the interface boundaries of media whose direct observation is impossible.
- The method may be useful in assessing the interfacial tensions arising in metallurgical systems, e.g. at liquid metal - liquid slag boundaries. The initial tests for Al - slag systems gave positive results.

- The problem of the relationship between adhesion work and adhesion force remains unexplained, nevertheless, further studies and experimental tests related to the physics of interfaces and the forces acting there should be justified and required.

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