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ASSESSMENT OF USABILITY OF MOLTEN SALT MIXTURES IN METALLURGY OF ALUMINUM ALLOYS AND RECYCLING OF COMPOSITE MATERIALS BASED ON THE MATRIX OF Al ALLOYS

OCENA PRZYDATNOŚCI STOPIONYCH MIESZANIN SOLI W METALURGII STOPÓW ALUMINIUM I RECYKLINGU MATERIAŁÓW KOMPOZYTOWYCH NA OSNOWIE STOPÓW Al

Effectiveness of the slags used in metallurgy of aluminum alloys and in recycling of composite materials containing these alloys depends on their surface properties at the phase boundaries they are in contact with. An index of surface properties of molten mixtures of slag-forming salts has been formulated. Its calculated values are compared with measured results of surface tension (liquid – atmosphere) and interfacial tension (liquid – liquid) in the considered systems. It was found that the index can be helpful for purposes of proper choice of the mixtures of slag-forming salts used both in Al alloys metallurgy and in recycling of composite materials based on the matrix of Al alloys.

Keywords: Fluxing agents, slags, Al alloys, refining and recycling, surface properties

Skuteczność żużli stosowanych w metalurgii stopów aluminium i recyklingu kompozytów z udziałem tych stopów, zależy od ich właściwości powierzchniowych na granicach faz, z którymi mają kontakt. Opracowano wskaźnik właściwości powierzchniowych stopionych mieszanin soli żużlotwórczych, a jego wyliczone wartości porównano z wynikami pomiarów napięć powierzchniowych (ciecz-atmosfera) i międzyfazowych (ciecz-ciecz) dla badanych układów. Stwierdzono, że wskaźnik ten może być przydatny w doborze mieszanin soli żużlotwórczych stosowanych zarówno w metalurgii stopów Al, jak i recyklingu materiałów kompozytowych na osnowie stopów Al.

1. Introduction

Two liquid phases: molton metal (or alloy) and slag occur in most metallurgical systems. The slag occurring at the surface of the metal bath not only protects it against negative atmospheric effects but also enables to make many treatments necessary to achieve good quality of the material designed for shaping the casted products. In the conditions of fully controlled process (e.g. melting or refining) the slag existing at the surface of liquid alloy is formed of molten slag-forming substances called fluxing agents. The fluxing agent used for purposes of metallurgical process is usually a mixture of chemical compounds that gets a single-phase liquid form in the temperature usually below the melting point of the processed metal or alloy. In case of e.g. refining flux the metallurgical system after the refining process includes a liquid refined alloy and liquid post-refining slag contaning substances transferred from refining metal bath. When the main aim of refining is to remove solid inclusions (e.g. oxides) from the metal bath, the process consists in emulsifying of the system (i.e. liquid metal – liquid slag), then the inclusions might be taken up by the liquid slag. The same mechanism occurs in recycling process of suspended composite materials, that consists in separation of the components and their conversion in the recycling system, i.e. transmission of solid phase particles from the suspension state in liquid metal matrix to suspension in so-called liquid recycling medium obtained in result of melting of the salt mixture.

The fluxing agents used in melting and refining of aluminum alloys should allow to obtain the slag which ensures [1,2,3]:

- permanent adsorption of solid inclusions suspended in metal bath to interphase surface between liquid metal and liquid slag;
- permanent adsorption of the inclusions to the slag, i.e. their passage through the interphase liquid metal – liquid slag surface;
- impeded emulsification of the system, i.e. the slag drops should remain in metal bath or metal drops in liquid slag.

The same conditions should be fulfilled by recycling media in the recycling processes of suspended composite materials.

In case of emulsified systems of liquid phases composed of a refined metal (or recycled composite suspension) and slag

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(the recycling medium) calculation of the changes in surface energy undergoing in particular stages of the (refining or recycling) process indicates that a critical stage of it occurs during transmission of the solid phase (the inclusion or reinforcing particle) to the slag or to the recycling medium, i.e. its passage through the interphase liquid metal – liquid slag surface (medium).

During de-emulsification of the post-refining or post-recycling (in case of a suspended composite material) system the calculation of the changes in surface energy of the system gives evidence that the variant of separation of liquid phases consisting in removing of slag (medium) drops from metal is much more advantageous than that in which metal drops are removed from the slag. This is important especially when determining the quantity (volume) of the medium used in recycling process of the suspended composite materials. In both variants the values of interfacial tension at the border between liquid metal and liquid slag (medium) are determinative for the process effectivness. The main problem in case of the slag (medium) drop leaving the metal is that the value of interfacial tension is rather unimportant, while in the opposite case the tension should be as high as possible.

In case of recycling of composite materials with suspended reinforcement the recycling medium should effectively replace the liquid composite matrix (e.g. the aluminum alloy) in the capillaries of a porous agent reinforcing the composite material. It means that the recycling agent should push out the liquid metal matrix from the capillaries. Spontaneous course of the process is conducive to negative balance of surface energy in the changing system. The value of interfacial tension between liquid matrix metal and liquid recycling medium is an important factor for the balance. In this case the lower interfacial tension the more efficient the course of the process [4].

Behaviour of the refining and recycling systems depends both on the values of interfacial tension arising at the interfaces of the phases occurring in the systems and on interrelation between these values. Some of the tension values (e.g. interfacial tension at the liquid – gas surface) are known or measurable. The others (e.g. interfacial tension between solid and liquid phases) may be calculated. The interfacial tension arising between liquid phases may be determined or estimated. In case of metallurgical systems determination of these tensions is methodically difficult considering the properties of both liquids (molten metal and liquid slag).

The most advantageous surface properties of liquid fluxing agents (slags) may be chosen experimentally, however, more accurate orientation of these highly time- and labour-consuming experiments is recommended. Therefore, an attempt is made to assess usefulness of the fluxing agents (recycling media) based on ionic theory of slags [5].

2. Metallurgical slags

In casting technology of aluminum alloys the mixture of molten salts are used as fluxing agents (recycling media). Chemical composition of some mixtures is specified, particularly in former literature references [6,7]. Nevertheless, these formulations are more and more frequently identified by their company names, while their manufacturers protect the recipes, (according to the market rulet). To very important properties of these liquid mixtures belong surface tension (liquid – atmosphere) and interfacial tensions at the border between liquid phases (liquid metal or alloy and the slag).

According to commonly assumed theory the slags occurring in the metallurgical systems are the liquids composed of simple and complex ions [8]. The theory says that surface tension of the slags depends on the force of attraction between ions and the type of chemical bonds. The metallic bonds typical for liquid metals are conducive to the fact that (metal) liquids are distinguished by the highest values of surface tension.

A measure of durability and power of these bonds is the value of ionic potential j, being an approximate measure of the bond energy, defined by the formula (1):

$$\varphi = \frac{Z}{r} \tag{1}$$

where:
Z – elementary ion charge (valence),
r – ionic radius [Å].

Since growing ionic potential causes the increase of surface tension [8], it may be assumed that reduced surface tension may be induced by the ions of possibly low charge and large ionic radius occurring in the slag. Moreover, it may be presumed that reduction of surface tension in the system composed of liquid flux (slag) and atmosphere should affect the change in interfacial tension of liquid alloy – liquid flux.

3. Estimation of flux agents used in metallurgy of aluminum alloys

The flux agents used in metallurgy of aluminum alloys are made of salt mixtures, mainly chlorides and fluorides. Their choice and use is conditioned by their many differentiated properties, e.g. solidification point, density, but also consistency, harmfulness or dangerous to the environment, etc.

In order to assess the relationship between chemical composition of the slag-forming salt mixture and surface tension of the liquid obtained from it the following operations were presumed:
- to determine ionic characteristics of selected slag-forming mixtures;
- to determine and assume the physico-chemical factor of surface properties of liquid (molten) mixtures;
- to verify experimentally the conclusions resulting from the calculation.

3.1 Chemical composition of the slag-forming mixtures

As it was mentioned above, among the most frequently used compounds of the slag-forming mixtures there are chlorides ($NaCl$, KCl, $MgCl_2$, $CaCl_2$ …) and fluorides (NaF, AlF_3, CaF_2, KF, AlF_6 …). Ionic characteristics of the selected mixtures were determined in the first stage, by calculation of ionic potential of the ions that are the most common

components of the slag-forming mixtures. Results of the calculation are specified in Table 1.

For the calculation purposes the predefined compositions of the mixtures were assumed (in weight percents) and, based on these data, the number of moles (n_i) of particular compounds (e.g. KCl, NaF) of the considered mixture and ionic fractions corresponding to them were calculated.

The number of moles of the mixture components were calculated from the relationship (2)

$$n_i = \frac{(\%)i}{Mi} \qquad (2)$$

where:
(%)i – percent fraction of the i component in the considered mixture;
M_i – molar weight of the i component.

TABLE 1

Ionic potentials of selected cations and anions, according to[9)]

Cation	Cation radius [Å]	Ionic potential φ	Anion	Anion radius [Å]	Ionic potential φ
Li+	0,76	1,32	OH-	1,37	0,73
Na+	1,02	0,98	F-	1,33	0,75
K+	1,38	0,72	Cl-	1,81	0,55
Mg+2	0,72	2,78	Br-	1,96	0,51
Ca+2	1,00	2,00	J-	2,16	0,46
Al.+3	0,54	5,56	O-2	1,40	1,43
Ti+2	0,86	2,33			
Ti3	0,67	4,48			
Ti+4	0,61	6,56			
Rb+	1,52	0,66			
Cs+	1,67	0,60			

The mole numbers of the mixture components (KCl, NaF, NaCl….) served as a basis for calculation of the numbers of moles of particular ions (e.g. K+, Cl-, F-…).

After calculation of the numbers of moles of particular elements (cations and anions) occurring in the mixture, the electrostatically equivalent ionic fractions were calculated ($X(+)$, $X(-)$) (according to Flood [5]):

$$X_{(+)} = \frac{Z_{(+)} \cdot n_{(+)}}{\sum Z_{(+)} \cdot n_{(+)}} \; , X_{(-)} = \frac{Z_{(-)} \cdot n_{(-)}}{\sum Z_{(-)} \cdot n_{(-)}} \qquad (3)$$

where
$n_{(+)}, n_{(-)}$ – numbers of moles of the ions of particular elements;
$Z_{(+)}, Z_{(-)}$ – absolute valency of the ions.

3.2 Surface property factor

As it was mentioned above, low value of surface tension of the slags is due to occurrence of the ions of small charge and large ionic radius in them. Taking into account small values of

ionic potentials, further consideration was carried out based on the potassium and sodium salts. Since among the most common salts of these elements there are chlorides (KCl and NaCl), it was presumed that the assumed surface property factor of the molten salt mixtures should be based on the values of ionic potentials of potassium and sodium cations (Table 1). The chlorine anions have lower ionic potential, nevertheless their predomination in molten mixtures (chlorides) restricts or even probably precludes clear differentiation of expected values of the factor that is a goal of the present consideration.

Hence, a sum of the products of ionic fractions of the cations occurring in the liquid mixture and their ionic potentials (4) is assumed to be the surface property factor of molten salt mixtures:

$$W = \sum X_{i(+)} \cdot \varphi_{i(+)} \qquad (4)$$

Table 2 specifies the values of the factor calculated for a set of 31 salt mixtures serving as fluxing agents or potentially designed for use in metallurgy of aluminum alloys. The first seven items of Table 2 represent compositions of the fluxing agents used in metallurgy of aluminum alloys, recommended by the guide-books and handbooks. It should be noticed that the preparation named POKAL, developed in Poland in the seventies of the 20th century, deserved for a very good opinion among the metallurgists. It was widely used in Polish foundries of aluminum alloys. Therefore, it may be considered as a good reference of usefulness of other slag-forming mixtures.

The data of Table 2 show that liquid mixtures of potassium and sodium chlorides are distinguished by decidedly the lowest values of the W factor. At the same time, the factor evidently decreases with growing KCl contents in the mixture (Table 2, p.8-17). Addition of sodium fluoride to KCl+NaCl mixture results in slight increase of the factor (Table 2, p.18-24), while in case of replacing sodium fluoride with aluminum fluoride (with similar KCl and NaCl contents) its value decidedly grows (Table 2, p.25-31). Compositions of the mixtures (Table 2, p.1-7) correspond to the values recommended in metallurgical practice of aluminum alloys, and the values of calculated W factors fall in wide range – its maximum level (2.2989) is nearly three times as high as the minimum equal to 0.7999. It should be underlined that an important feature of slag-forming mixtures, not related to the W factor, is the temperature or temperature range of their liquidity. The mixture of the salt No 17 solidifies in the range of 750-734ºC. Therefore, it cannot be considered to be useful in metallurgy of circum-eutectic aluminum alloys, since their melting points are significantly lower.

4. Preliminary verification attempts

Measurement of interfacial tension of molten salt mixtures at the border with atmosphere and, particularly, with liquid alloy, is methodically difficult (due to aggressive environment and high temperature). Moreover, even small change in temperature of the system may affect the values of the obtained results.

TABLE 2

Calculated values of the surface property index of molten salt mixtures

Item	Chemical composition of the salt, expressed in [mass fraction]						W factor	Notes
	KCl	NaCl	Na₃AlF₆	AlF₃	NaF	CaF₂		
1.	80	-	-	-	20	-	0,7999	[6,7] (635°C)
2.	50	15	35	-	-	-	2,2989	[10] (625°C)
3.	50	20	-	-	30	-	0,8790	[6,7]
4.	45	45	-	-	10	-	0,8825	[6,7] (610°C)
5.	43	42	15	-	-	-	1,5056	[10] (635-620°C)
6.	25	60	15	-	-	-	1,5498	[6,10] (690-630°C)
7.	45	46	1	-	5	3	0,9725	POKAL
8.	80	20	-	-	-	-	0,7828	
9.	75	25	-	-	-	-	0,7975	
10.	70	30	-	-	-	-	0,8158	
11.	65	35	-	-	-	-	0,8258	
12.	60	40	-	-	-	-	0,8394	
13.	55	45	-	-	-	-	0,8527	
14.	50	50	-	-	-	-	0,8657	[10] (655°C)
15.	45	55	-	-	-	-	0,8783	
16.	40	60	-	-	-	-	0,8907	
17.	33	67	-	-	-	-	0,9067	[10] (750-734°C)
18.	49	50	-	-	1	-	0,8686	
19.	49	49	-	-	2	-	0,8691	
20.	48	49	-	-	3	-	0,8755	
21.	47	48	-	-	5	-	0,8755	
22.	45	45	-	-	10	-	0,8755	
23.	43	42	-	-	15	-	0,8892	
24.	40	40	-	-	20	-	0,8977	
25.	49	50	-	1	-	-	0,9754	
26.	49	49	-	2	-	-	1,0797	
27.	48	49	-	3	-	-	1,1833	
28.	48	47	-	5	-	-	1,3799	
29.	45	45	-	10	-	-	2,0341	
30.	43	42	-	15	-	-	2,2382	
31.	40	40	-	20	-	-	2,5762	

Using the stand (crucible furnace, dynamometer with tester ring on mobile traverse and recording devices) designed for estimation of interfacial tension values of the systems composed of liquid aluminum alloy – liquid salt mixture – atmosphere [11] and verified measurement method [12] (Du Noüy ring method) preliminary tests of determination of interfacial tension values in the considered system have been carried out, for molten mixture of two salts (KCl and NaCl), with varying proportion of them. The equilibrium plot of the system KCl + NaCl shows that solidification points of mixtures No 1 and 3 (Table 3), while in case of the mixture No 2 the solidification point is slightly lower [13]. Results of these tests are shown in Table 3 and Fig. 1.

TABLE 3

Values of measured interfacial tensions in the considered systems

Item	Molten salt mixture [mass fraction]	Interfacial tension [mN/m] at the border with	
		air	aluminum alloy
1.	40 KCl + 60 NaCl	107±16 (8)	297±76 (16)
2.	50 KCl + 50 NaCl	120±11 (30)	233±39 (10)
3.	60 KCl + 40 NaCl	99±9 (24)	222±57 (17)

() – the numbers of carried out tests specified in brackets

In spite of significant standard deviations of the average values specified in Table 3 an explicit drop of measured

tension values is observed (both at the border between liquid salt mixture and air as well as with liquid aluminum alloy) with growing KCl contents in the considered salt mixtures. As a consequence the surface property factor W also decreases. The case of the salt mixture No 1 at the border with air (that is not consistent with the above conclusion) may be a result of lower number of tests or another reason unknown to the authors. Nevertheless, the conclusion resulting from the interfacial tension values registered in the other tests and their relationship with W factor remains valid. The relationship is particularly clear in case of interfacial tension at the borders between molten salts and liquid aluminum alloy. It is worthy to notice that they are 3-4 times lower as compared to the tension between liquid aluminum and gas atmosphere [14].
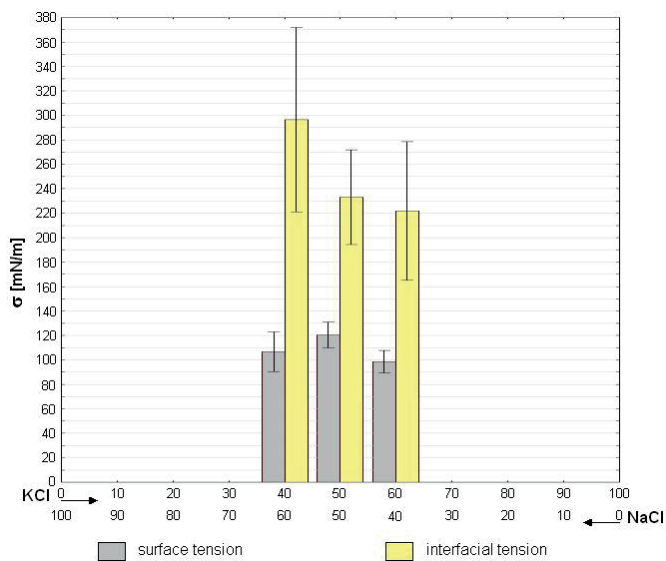

Fig.1. The measured interfacial tension values of molten salt (KCl+NaCl) mixtures of different composition fractions

5. Conclusions

In metallurgy of aluminum alloys the temperature range, in which particular treatments and processes are carried out, is of absolute priority considering the choice used of fluxing agents. Their evident liquidity under the conditions of metallurgical processing of the alloys is required necessarily. Nevertheless, the range is so broad that composition of the salt mixtures may be so adjusted as to maximize the metallurgical effects (melting, refining, recycling). The results of calculations and verification tests enable to formulate the following conclusions:

1. The calculations give clear evidence of the relationship between the value W of assumed factor of surface properties of the slag-forming mixtures and their chemical composition.
2. High potassium chloride contents of the slag-forming mixture is conducive to reduction of the W factor.
3. Occurrence of aluminum fluoride (AlF_3) and cryolite in the mixture decidedly increases value of the factor, while sodium fluoride (NaF) plays less significance role.
4. Results of preliminary verification tests indicate that the drop of the W factor in considered mixtures is due to decreased interfacial tension at the border of molten mixture and liquid aluminum alloy.
5. Explicit changes in interfacial tension values which are accompanied by only slight changes of the W factor suggest that it may serve for determining the direction of the changes in surface properties of slags in metallurgy of aluminum alloys.
6. Effectiveness of the POKAL (tested in metallurgical practice) allows to presume that the factor of surface properties of molten slag-forming mixtures should not exceed the level of 1 (W≤1.0).

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