Temperature dependences of wetting angles of steel 12Cr18Ni9Ti and ceramics by the melts with least additions of alkali metals

M M Gubzhokov1, M Kh Ponegev1, A B Sozaeva1 and V A Sozaev2

1 Kabardino – Balkarian State University, Nalchik, ul. Chernyshevskogo, 173, 360004, Russia
E-mail: sozaevv@kbsu.ru

2 North Caucasus Mountain and Mining Institute; sozaevv@kbsu.ru

Abstract. Temperature dependences of wetting angles of 12Cr18Ni9Ti steel and PZT ceramics by the melts with least additions of alkali metals were studied in a wide temperature range in helium atmosphere. The temperature thresholds of wetting were found on the dependences when In–Na melts wet the 12Cr18Ni9Ti steel. Observed thresholds have been studied versus the concentration of sodium in indium. The sudden decrease in wetting angles was also observed at 650–700°C if substrate used was the PZT piezo-ceramics. Similar features were not detected at wetting the same materials by Cd–Na and Pb–Li melts.

1. Introduction

Alkali metals possess low surface energy and high activity therefore their least additions to melts can considerably modify their physicochemical properties.

In contrary to the melts of alkali metals the concentration dependences of surface properties of alloys containing alkalis are studied predominantly in limited concentration intervals, more often at minimal additions. The number of studied systems is rater limited too [1,2]. The studies of surface properties in lead–lithium alloys are of special interest. The lead–lithium melts of pre–eutectic and eutectic compositions are promising as heat carriers in nuclear power plants [3–6]. The studies of surface properties of alloys containing least additions of alkali metals are also important for devising novel high–active solders and systems of metallization. However, surface properties of alloys including alkalis are studied insufficiently.

The most difficult part of such investigations is that alkali or alkali – earth metal additions may “burn out” during the isothermal exposure. This “burning out” usually appears if measurements are carried out on the metal – vacuum boundary and not in inert atmosphere. When a researcher measures wetting angles the vaporized high active metals may condensate on the substrate and metallic drop would in fact wet a heterogeneous surface. This is a source of possible artifacts.

So, we studied temperature dependences of wetting angles between the 12Cr18Ni9Ti steel and indium – sodium, cadmium – sodium, lead – lithium melts and between the lead–zinc–titanium (PZT) piezo-ceramics and indium – sodium melt.
2. Experimental
Pure samples of In, Cd, Pb, Na and Li were alloyed with use of master alloys in glass ampoules in helium atmosphere [7] to obtain solid solutions In–Na, Cd–Na, Pb–Li of a given concentration. The temperature dependence of wetting angle was studied on the samples which were cut from the ingots taken out of ampoules after solidification. The concentration of solid solutions thus obtained was measured by the residual resistance. Samples of solid solutions were kept in vacuum oil VO–1 before the measurements.

The substrates of 12Cr18Ni9Ti steel and PZT piezo-ceramics were polished and washed in pure alcohol and distilled water before experiments.

The measurements of the wetting angle $\theta$ between the steel or ceramics and melts were performed using the sessile drop method in helium atmosphere. The profiles of the drops were framed by digital camera Kodak (6.1MP) and Pentium4 computer was used for processing and analyzing the data. The drop was exposed at constant temperature during 10 minutes before taking the picture. The coefficient of expansion was determined after each measurement by comparing the diameter of cold drop and its image. The error in defining the wetting angle was of 1.3%.

3. Results
3.1. The steel 12Cr18Ni9Ti wetted by indium–sodium melts
The results for temperature dependences of the wetting angle $\theta$ between 12Cr18Ni9Ti steel and In–Na melts are presented in Figure 1.

![Figure 1. The temperature dependence of edge wet angle between 12Cr18Ni9Ti steel and the following melts: 1 – In, 2 – In+0.02 at.% Na, 3 – In+0.1 at.% Na, 4 – In+0.3 at.% Na, 5 – In+0.5 at.% Na.](image)

One can see from the Figure 1 that In–Na melts do not wet the steel at melting point ($\theta>100^\circ$). Values of wetting angles decrease with the temperature raise and drop in $\theta$ appears at certain temperatures. This means that the indium – sodium melts begin to wet the surface of the steel (angles $\theta$ become almost immeasurable here).

Figure 1 shows that observed thresholds of wetting depend on the concentration of sodium in indium. The general picture is the following: the more is sodium concentration the less is the “threshold” temperature, except the In–0.02 at.% Na system. The latter can be explained by the concentration dependence of the surface tension of indium – sodium melts shown in Figure 2. These experiments were performed using the sessile drop method on graphite substrates at 800°C. One can observe a minimum at $x=0.02$ at.% on the dependence. The surface tension, in turn, determines the motive force of spreading, which referred to the unit of length of wet perimeter is defined at limited spreading as [8]:

$$\Delta \sigma = (\sigma_{SG} - \sigma_{SL}) - \sigma_{LG} \cos \theta_D,$$  \hspace{1cm} (1)
where \( \theta_D \) is the dynamical time–dependent wetting angle between solid and liquid, \( \sigma_{LG}, \sigma_{SG}, \sigma_{SL} \) are the interfacial tensions on the boundaries liquid–gas, solid–gas and solid–liquid, respectively.

One can see from Figure 1 that wetting angles between the 12Cr18Ni9Ti steel and In–Na melts of various concentrations are quite close. Hence, according to the equation (1), the motive force of the spreading increases with decrease of \( \sigma_{LG} \) resulting in the shift of the threshold of wetting for the melt.

The very existence of the thresholds can be explained by the partial dissolution of the substrate in liquid melts [9–11]. The edges of a crater formed are barriers for the spreading. The motive force \( \Delta \sigma \) increases with increase in temperature up to the critical value sufficient for this barrier overcoming.

### 3.2. The 12Cr18Ni9Ti steel wetted by lead–lithium melts

Wetting of the steel enriched in chromium (FeCr 8at.%) was studied in [3–6]. It was shown that the wetting angle was of 68 degrees at 400°C on the surface of the steel after mechanical polishing by a diamond paste. The wetting angle decreased down to 60 degrees after thermal treatment of the steel substrate at 850–900°C in vacuum because of destruction of chromium oxide film on the contact surface.

The wetting of the 12Cr18Ni9Ti steel was studied insufficiently.

The results of our study of wetting the steel by lead–lithium melts are given in Figure 3. One can see that temperature dependences of wetting angles in this case are linear. The wetting angles decrease with temperature raise.

![Figure 3](image-url)
Though wet angles decrease with temperature raise there is no wetting before 1000°C (θ>π/2). One should notice that in this case the substrates were not preliminary heated in vacuum at 650–900°C, as it was done in [9].

3.3. The 12Cr18Ni9Ti steel wetted by cadmium–sodium melts
There is no reported data on wetting of chromium containing steels by Cd–Na melts. Therefore, we have studied temperature dependences of wetting angles between the 12Cr18Ni9Ti steel and Cd–Na melts in temperature range from melting point up to 600°C. Steel substrates were not preliminary heated at T>850°C. Results of the measurements are presented in Figure 4. One can see that in this case temperature dependences of wetting angle are linear. The wetting of the steel (θ<π/2) starts at a temperature of 550°C in the case of Cd–0.069 at.% Na melt and at a higher temperature in the case of Cd–0.24 at.% Na melt.

Figure 4. Temperature dependences of wetting angle between the 12Cr18Ni9Ti steel and the following Cd–Na melts: 1 – 0.01 at.%Na, 2 – 0.036 at.% Na, 3 – 0.48 at.% Na, 4 – 0.24 at.% Na, 5 – 0.069 at.% Na.

Coefficients of linear approximation of the temperature dependences of wetting angles obtained by the least squares method are shown in Table 1.

| No | melt           | A, degrees | B, degrees/°C |
|----|----------------|------------|---------------|
| 1  | Pb 0.03 at.% Li | 133        | 0.0081        |
| 2  | Pb 0.1 at.% Li  | 142        | 0.0223        |
| 3  | Pb 0.3 at.% Li  | 125        | 0.0078        |
| 4  | Pb 0.5 at.% Li  | 132        | 0.0244        |
| 5  | Cd 0.01 at.% Na | 152        | 0.0802        |
| 6  | Cd 0.036 at.% Na| 146        | 0.0803        |
| 7  | Cd 0.48 at.% Na | 139        | 0.0777        |
| 8  | Cd 0.24 at.% Na | 129        | 0.0747        |
| 9  | Cd 0.069 at.% Na| 126        | 0.0835        |
3.4. The PZT piezo-ceramics wetted by indium–sodium melts

The finding of a low – temperature techniques for the metallization of ceramics is especially important for functional ceramics (for example, piezo-ceramics) because the low – temperature metallization allows keeping certain surface structures and properties. That is why here we study wetting of a surface of the PZT piezo-ceramics by In–Na melts.

Temperature dependences of wetting angles for this case are presented in Figure 5.

![Figure 5. The temperature dependences of wetting angle between the PZT ceramics and the following In–Na melts: 1 – In, 2 – In+0.02 at.% Na, 3 – In+0.1 at.% Na, 4 – In+0.3 at.% Na, 5 – In+0.5 at.% Na.](image)

It is seen from Figure 5 that the dependences obtained in our study are linear until the temperature of 650°C after which they fall. The best wetting is observed in the case of In–0.02 at.% Na melt. However we do not see a distinct dependence of the wetting “threshold” on Na concentration.

4. Conclusions

The temperature dependences of wetting angles between dilute liquid solutions In–Na, Pb–Li and Cd–Na (alkalis being added below the solubility limit in solid state) and the 12Cr18Ni9Ti steel were measured for the first time. These dependences are linear in the case of Pb–Li and Cd–Na melts.

The temperature thresholds of wetting were found in the case of In–Na melts and their dependence on sodium concentration was revealed. The temperature of abrupt decrease in wetting angle decreases with sodium content increase. The In–0.02 at.% Na melt is an exception which correlates with the minimum on the concentration dependence of the surface tension at $x_{Na}=0.02$ at.%.

The temperature dependences of wetting angles between In–Na melts and PZT piezo-ceramics are studied for the first time too. The sudden decrease in wetting angles appears above 650°C. The maximal drop in the angles $\theta$ is observed in the case of In–0.02 at.% Na melt.

References

[1] Alchagirov B B Obzori po teplofizicheskim svoistvam veschestv, (Moscow: IVTAN 1991) 3(89) and 4(90), 178 p. [in Russian]
[2] Alchagirov B B and Khokonov Kh B Teplofizika visokih temperatur, 32(5) 756–783 (1994) [in Russian]
[3] Eustathopoulos N, Nicholas M and Drevet B Wettability High Temperatures (Netherlands, Elsevier: 1999) 418 p.
[4] Schulz B Fusion Engineering and Design 14 199–205 (1991)
[5] Glasbernner H, Konys J and Voss Z J. on Nuclear Materials 281 225–230 (2000)
[6] Protsenko P, Terlain F, Jeymond M and Eustathopoulos N., 10th Int. Conf. on Fusion Reactor Materials (Baden–Baden, Germany, 14–19 October 2001)

[7] Aleksandrov B N and Dalakova N V FMM 64(3) 464–474 (1987) [in Russian]

[8] Summ B D and Goryunov Yu V, Fiziko – himicheskie osnovi smachivania i rastekania (Moscow: Himia 1976) 231 p. [in Russian]

[9] Alchagirov B B, Novosadov V S, Radkovsky S G and Khokonov Kh B / In: Fizicheskaia himia granic razdela kontaktiruyuschih faz (Kiev: Naukova Dumka 1976) 103–107 [in Russian]

[10] Naidich Yu V Kontaktiny iavlenia v metallicheskih rasplavah (Kiev: Naukova Dumka 1972) 196 p. [in Russian]

[11] Novosadov V S, Petrunin I E, Shein Yu F and Konvisher B S / In: Smachivaemost i poverhnostnie svoistva rasplavov i tverdih tel (Kiev: Naukova Dumka 1972) 53–56 [in Russian]