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Preparation of diffusion coatings in ion-electron melts

Anfinogenov A. I., Chebykin V. V., Chernov Ya. B.

(Institute of High-Temperature Electrochemistry, Ural Division of RAS, Ekaterinburg 620219, Russia)

Abstract: A procedure of Ni, Cr, Mn, Co, and Mo (Me) transfer onto iron substrate in ionic-electronic melts LiCl-Li, $CaCl_2$-Ca, and $BaCl_2$-Ba was elaborated and the transport processes were studied. The saturated vapor pressure of these ionic-electronic melts is as low as enabled working at atmosphere pressure in an inert media up to 1000 ℃.

Armco iron was used as a substrate because it practically does not interact with lithium, calcium, and barium. The metals-diffusants were put into the melts in the form of a powder. The complete saturation of the melts with lithium, calcium, and barium was ensured by a preceding contact of a molten salt with an excess of Li, Ca, or Ba before loading of iron.

The reactions take place despite the metals and iron were separated from each other by the molten salt. The quantity of the metals transfered was determined by the change in mass before and after experiments, by microprobe analysis, and x-raying of the iron surface layer. The experiments were carried out at 900, 950 and 1000℃ during 5, 10, 15 and 20 hours.

At the first stage of the process the formation of the ionic-electronic melt occurs. For example, dissolution of calcium in the case of the system $CaCl_2$-Ca is mainly proceeded in the form of one-valent cations: $Ca + Ca^{2+} \leftrightarrow Ca^{+}$. As soon as the metal-diffusance is immersed into the melt, its dissolution in the form of negative ions takes place: $Me + Ca^{+} \leftrightarrow Me^{-} + Ca^{2+}$. In the vicinity of the iron substrate the last equilibrium will shift to the left generating a solid solution or intermetallide. The thickness of the diffusion layer rises as the temperature and saturation time increase. The obtained coverings were 20-60 (m thick, and their surface layer contained 15%-80 % (mass fraction) of the metal-diffusance.

Both the composition of the melt and the procedure of the coverings preparation in ionic-electronic melts have been patented (Patent RU2058422, 1996, pr. 30.09.93).

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Researchers at the Institute of High-Temperature Electrochemistry, Ural Division RAS, study isothermal transport reactions of metals in ion melts using a no-current method[1, 2]. The motive force of these reactions is the Gibbs energy of the alloy formation. Ion-electron melts served as the transport media for synthesis of diffusion coatings in this study.

Olshansky[3] was the first to introduce the term "an ion-electron melt". At present this type of melts also includes solvent melts of alkali and alkali-earth metals in their halogenides since these dissolved metals dissociate to cations and delocalized electrons:

$$Me \leftrightarrow Me^{n+} + n\,e^{-}. \tag{1}$$

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As a result, the electron conduction appears and increases with the concentration of the dissolved metal in these melts. Thus, ion-electron melts are intermediate between ion and metal (electron) melts. Some indirect experimental and theoretical results suggest that large concentrations of negative ions of many chemical elements, including d-metals, can be formed in ion-electron melts. It should be stressed that their concentrations are sufficient for realization of various physicochemical processes, which lead to the formation of diffusion surface alloys or protective and functional coatings.

Basic processes, which take place in such media, can be depicted schematically as follows. An ion-electron melt is formed at the first stage. For example, calcium dissolves predominantly as univalent cations in the $CaCl_2$-Ca system:

$$Me + Me^{2+} \leftrightarrow 2\ Me^{+}. \qquad (2)$$

When a d-metal or another element is submerged into this melt, it dissolves and forms negative ions (for example, Ni^-):

$$Ni + Me^{+} \leftrightarrow Ni^{-} + Me^{2+}. \qquad (3)$$

The last equilibrium shifts to the left near the iron substrate, which forms a solid solution with the dissolved element (Ni):

$$\begin{array}{rcl} | & Ni\rightarrow & | \\ Ni| & & |Ni\text{-}Fe \\ | & Me^{2+}\leftrightarrow Me^{+} & | \end{array} \qquad (4)$$

The present study deals with the isothermal transport of some d-metals in LiCl-Li, $CaCl_2$-Ca and $BaCl_2$-Ba melts. In this case, diffusant elements are transported in the direction from the more to less soluble element. The isothermal transport of metals in ion-electron melts is followed by the formation of diffusion alloy coatings. The transport of Ni, Cr, Mn, Co and Mo to the Armco iron was studied and a technology for synthesis of metal coatings of these metals was proposed.

The metal transport was studied by analyzing diffusion layers on cross-sections. Metallographic, X-ray phase and X-ray microspectrum analysis methods were used.

LiCl-Li, $CaCl_2$-Ca and $BaCl_2$-Ba melts were chosen as the objects of study, because their saturated vapors have a low pressure at temperatures of up to 1000 ℃ and, therefore, the melts can be handled at the atmospheric pressure. The substrate metal was Armco iron, because it interacts little with lithium, calcium and barium. The transported powdered diffusant metals Me_1 and the iron samples were spatially separated with the ion-electron melt:

$$Me_1 \mid MeCl_{(liq)} + Me_{(s)} + Me_1(s) \mid Fe. \qquad (5)$$

According to (4) the maximum solubility of lithium in its chloride melt is 1.28% (800 ℃), 1.67% (900 ℃), 1.84% (950 ℃) and 2.0% (1000 ℃) (mole fraction).

Thickness of the diffusion coatings on the Armco iron in LiCl-Li, $CaCl_2$-Ca and $BaCl_2$-Ba melts is given in the Table.

Considering the specific increase in the mass of the substrate sample, which characterizes, as the first approximation, the transport intensity in the LiCl-Li melt, the transported metals can be arranged in the series:

$$Mn = Ni > Co = Cr \approx Mo \rightarrow Fe. \qquad (6)$$

With respect to their solubility in pure lithium at 900-1000 (C, the diffusant metals are arranged in the series[5]:

$$Mn > Ni > Co > Cr > Fe > Nb > Mo > Ta > W. \qquad (7)$$

It is seen from the comparison of the series (6) and (7) before iron that they are identical, except molybdenum. The transport of molybdenum to iron can be explained by the fact that the solubility of Mo in Li is 10 times larger if lithium is contaminated with nitrogen [5].

According to (6), among the metals under study, molybdenum has the largest coefficient of diffusion to iron ($D_{Mo} = 1.95\times10^{-12}$ cm^2/s at 950℃).

The solubility of nickel in the LiCl-Li melt was 2.8×10^{-3}%- 5.0×10^{-3}% (mass fraction) at 800-950 ℃. The solubility of the other elements at 900 ℃ was 2.0×10^{-3}% (mass fraction) for cobalt and chromium, 5.0×10^{-3}% (mass fraction) for manganese, and 3.0×10^{-3}% (mass fraction) for molybdenum.

Table1 Thickness of coatings (μm) on the Armco iron in LiCl-Li, $CaCl_2$-Ca and $BaCl_2$-Ba melts

T/℃	τ/h	LiCl-Li					$CaCl_2$-Ca			$BaCl_2$-Ba		
		Ni	Mn	Co	Cr	Mo	Mn	Cr	Mo	Ni	Cr	Mo
900	5	23	22	18	16	25	—	—	—	—	—	—
	10	32	32	25	22	35	—	—	—	—	—	—
	15	39	39	34	27	43	—	—	—	—	—	—
	20	46	45	36	31	50	—	—	—	—	—	—
950	5	25	25	22	20	27	25.6	2.7	55	3.8	2.9	39
	10	35	35	32	28	39	36.3	3.8	60	5.4	4.1	55
	15	43	43	39	35	48	44.5	4.6	78	6.6	5.0	68
	20	50	50	45	40	58	51.5	5.4	85	7.6	5.8	78
11000	5	28	29	28	25	31	—	—	58	8.0	6.7	58
	10	40	41	39	36	44	—	—	65	11.4	9.5	82
	15	49	50	48	44	54	—	—	—	14.0	11.6	100
	20	56	58	55	51	63	—	—	115	16.0	13.4	116

It is seen from the series [7] that Nb, Ta and W are less soluble in lithium than iron. This observation may explain the fact that diffusion coatings of these metals were not deposited on iron in the LiCl-Li melt. Thickness of the diffusion layer increased with the temperature. Maximum concentrations of the diffusant metals on the surfaces of the iron samples were 50%-60 % Ni (mass fraction), 45%-60 % Mn (mass fraction), 18%-20 % Cr (mass fraction), 10%-18 % Co (mass fraction), and 55%-62 % Mo (mass fraction).

According to [7], the solubility of Ca in $CaCl_2$ is 3.26 % and 3.60 % (mass fraction) at 900 ℃ and 940 ℃, respectively. We used saturated $CaCl_2$-Ca solutions and brought the salt melt in contact with excess calcium. All parameters of the metal mass transfer in this melt were smaller than those in the LiCl-Li melt, while the transfer of Cu, Ni and Pd to iron and titanium was not detected.

The experiments in the $CaCl_2$-Ca melt demonstrated that the layer thickness was 30% smaller than that in the LiCl-Li melt. This fact might be due to the smaller solubility of the diffusant metals in the $CaCl_2$-Ca melt. For example, at 900 ℃ the solubility of Mn was 2.0×10^{-3}% (mass fraction) in the $CaCl_2$-Ca melt and 5.0×10^{-3}% (mass fraction) in the LiCl-Li melt.

The phase composition of the diffusion layers in the quickly quenched samples comprised substitutional γ solid solutions of (Mn)Fe and (Ni)Fe (austenite), α-(Cr)Fe and α-(Co)Fe (ferrite), and Fe_7Mo_3, Fe_3Mo, Fe_2Mo and FeMo intermetallics.

At 950 ℃ the chromium weight increment in the $BaCl_2$-Ba melt differed little from that in the $CaCl_2$-Ca melt, whereas the surface concentration of chromium was nearly 2 times higher than its concentration in the $CaCl_2$-Ca melt. The solubility of nickel and chromium in the $BaCl_2$-Ba melt was 3.2×10^{-3}% (mass fraction) at 950 ℃ and 3.5×10^{-3}% (mass fraction) at 1000 ℃, respectively. The mass transfer of V, Pd, Nb, Ta and W to iron was not detected.

A patent covering the method and the melt composition for deposition of metal coatings was issued [8].

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