ELECTROLYTIC SEPARATION FOR Ce-CARBIDE AND Fe-Ce-CARBIDE IN STEEL①

Xiao, Qiang Han, Qiyong
Department of Physical Chemistry,
University of Science and Technology Beijing, Beijing 100083
Ding, Shijie
Beijing University of Chemical Technology

ABSTRACT The possibility of separating RE-carbide by electrolysis was discussed on the basis of electrolyte contrast, magnetic separation and X-ray diffraction analysis. The experiments showed that the electrolyte consisting of 1%LiCl+5%$N(CH_2CH_2OH)_3$+5%$C_2H_6O_2$+89% anhydrous CH_3CH_2OH was appropriate for the electrolytic separation of Ce-carbide and Fe-Ce-carbide. And it was found that when the content of cerium in the steel exceeded a certain amount, $Fe_2Ce_2C_3$ and Ce_2C_3 would be formed in sequence with the increase of the content of carbon.

Key words: Ce-carbide Fe-Ce-carbide electrolytic separation

There has been a great divergence of views on whether RE elements can form its carbides in the steel and whether RE-carbides has any influence on the matrix structure. It is well-known that RE has certain solubility in the steel, and especially when the content of oxygen and sulphur is quite low, there will be some interaction between the dissolved RE and the other alloying elements. Because carbon is an important element in the steel, the interaction between RE and carbon will undoubtedly affect the structure and property of the steel. Although some experiments have shown the indication of the interaction between RE and carbon[1], until now there have been few reports for explaining what kind of interaction between RE and carbon is and what the product is. Since RE content (including RE metallic compounds) is rather low, generally several hundred ppm, and RE-carbide is extremely unstable and can be decomposed in air and even more can not exist in water, thus the past experiments by means of ion microprobe, AES (Auger electron spectroscopy) and TEM, etc., have never directly obtained the experimental data to prove the existence of Ce-carbide in the steel[2].

Therefore, in this paper, we tried to find an appropriate electrolyte to separate RE-carbide and to ensure RE-carbide not to be decomposed. Thus it provided the basis for further proving the existence of RE-carbide in the steel.

1 EXPERIMENTAL METHOD

For investigating the behaviour of RE-carbide in the electrolyte, it must be first to ensure the formation of RE-carbide in the melted samples. Thus the amount of carbon and cerium in the samples has been enhanced respectively. The samples were melted in carbon tube furnace and their chemical composition was listed in Table 1. Since the carbon content of the samples was quite high (according to T8 and T 12 steel), and the cerium content was far beyond the common extent, thus in this condition the RE-carbide would be formed[3]. Then the samples were forged to the experimental bars of d12 mm and were

① Received Nov. 7, 1993; accepted in the revised form Mar. 3, 1994.

Table 1 Chemical Composition of Samples (wt. -%)

Samples	C	Si	Mn	S	Ce
A	1.22	0.25	0.87	0.0126	0.25
B	0.80	0.49	1.09	0.0180	0.32

normalized at 860 ℃ for 1.5 h.

According to the RE phase electrolytics basic experiments[4], the following two electrolytes were tried.

(1) 1%$(CH_3)_4NCl$+5%$N(CH_2CH_2OH)_3$+5%$C_3H_5(OH)_3$+89% anhydrous CH_3OH

(2) 1%LiCl+5%$N(CH_2CH_2OH)_3$+5%$C_2H_6O_2$+89% anhydrous CH_3CH_2OH

The samples were electrolysed at the current density of 25mA/cm^2 and temperature of −10 ℃. During the electrolysis, since the electrolytic potential difference of RE phase (except for RE_2Fe_{17}) and the matrix was quite large[4-5], thus the RE inclusions could be seperated from the electrolytes.

After electrolysis was completed, the amounts of rare earth in solid solution in the steel were determined by ICP spectroscopic analysis. The experimental error was less than 1×10^{-4}%. Since the mixture of carbides and inclusions from the electrolysis could only be obtained, thus it would be very difficult to separate carbides from inuclsions completely by chemical means. And the decomposition of inclusions could hardly be avoided, so it could not be determined whether the detected RE in the separated carbides was from the RE-carbides or the product of decomposed inclusions. Therefore, no matter which anhydrous electrolyte was chosen, it was difficult to extract the carbides by the only means of chemistry. Thus, according to the magnetic property of cementites and Fe-RE-carbides, magnetic separation was further used to separate carbides from sulfide of RE, oxysulfides of RE and oxide of RE. Finally, X-ray diffraction analysis was used. Throughout all of above procedures, oxidation and hydrolysis should be prevented.

2 RESULTS AND DISCUSSION

The results of determination of the amounts of Ce in the solid solution were shown in Table 2. It could be found that the amount of Ce in the solid solution of electrolyte 1 obviously trended towards high and was far beyond that of electrolyte 2. This indicated that several RE phases might have been decomposed and could not be separated from the matrix and thus the amount of Ce in the solid solution seemed to be unusually high. Whereas in electrolyte 2, the dielectric constant of the solvent, ethanol, was smaller and its chemical ability seemed rather weaker than that of methnol. And 1, 2-ethandiol was a reducing agent, which could consume the oxygen in the electrolyte and reduce the oxidation and decomposition of the extracted phase. For above reasons, the dissolving and damage of RE phase was small and the percentage of extracted carbides was high, thus the carbides could be reserved more completely. Therefore, the amount of Ce in the solid solution in electrolyte 2 was about 0.002 wt.-% which seemed quite low.

Table 2 Solid Solubility of Cerium in the Steel (wt. -%)

Samples	Electrolytes	Amount of Ce in the solid Solution	
		First determination	Second determinatior
A	1	0.0156	0.0159
A	2	0.00224	0.00202
B	1	0.0180	0.0193
B	2	0.00201	0.00257

The data of X-ray diffraction analysis showed that no diffraction peaks of Ce-carbides appeared for the samples treated by electrolyte 1. Whereas for other two samples treated by electrolyte 2, $Fe_2Ce_2C_3$ was found (see Table 3) and furthermore, Ce_2C_3 existed in sample A (see Table 4). And if the separated inclusions were put into water, an intense smell of acetylene could be felt.

All of above results indicated that RE-carbides could be separated without being decomposed in electrolyte 2, and both Ce-carbide and Fe-Ce-Carbide could be decomposed in electrolyte 1 and thus could not separate from the matrix, so as to cause the amount of Ce in solid solution to become high. Therefore, Electrolyte 1 was not appropriate for extracting all of RE phase and seperating them from the RE in solid solution.

Table 3 X-Ray Diffraction Data of $Fe_2Ce_2C_3$

Inclusions		Standard Value[3]		Inclusions		Standard Value[3]	
d/Å	I/I_1	d/Å	I/I_1	d/Å	I/I_1	d/Å	I/I_1
3.341	s	3.340	s	1.711	w	1.721	w
3.045	w	3.050	w	1.700	w	1.697	w
2.810	s	2.828	m	1.633	w	1.636	m
2.694	m	2.732	m	1.448	w	1.445	w
2.654	m	2.639	m	1.426	w	1.436	w
2.455	s	2.495	s	1.347	w	1.347	w
2.264	w	2.249	w	1.328	w	1.339	w
2.218	w	2.205	w	1.297	w	1.307	w
1.932	w	1.932	m	1.195	w	1.202	m
1.851	w	1.843	w	1.162	w	1.170	m
1.821	w	1.818	w	1.141	w	1.139	w
1.764	w	1.768	w				

note: s—strong; w—weak; m—mid

Table 4 X-Ray Diffraction Data of Ce_2C_3

Inclusions		ASTM 20-261		Inclusions		ASTM 20-261	
d/Å	I/I_1	d/Å	I/I_1	d/Å	I/I_1	d/Å	I/I_1
3.421	w	3.420	40	1.547	w	1.540	70
2.955	s	2.980	90	1.448	w	1.447	40
2.645	s	2.660	90	1.347	w	1.368	40
2.264	m	2.280	70	1.328	w	1.334	30
2.107	w	2.110	30	1.297	w	1.304	70
1.821	w	1.798	60	1.260	w	1.240	40
1.721	w	1.721	40	1.219	w	1.220	40
1.649	m	1.653	100	1.195	w	1.195	40

note: s-strong; w-weak; m-mid

3 CONCLUSIONS

(1) Electrolyte consisting of 1%LiCl + 5%$N(CH_2CH_2OH)_3$ + 5%$C_2H_6O_2$ + 89%anhydrous CH_3CH_2OH was appropriate for the separation of Ce-carbide and Fe-Ce-carbide.

(2) When the content of Ce exceeded a certain amount in the steel, $Fe_2Ce_2C_3$ and Ce_2C_3 could be formed in sequance with the increase of content of carbon.

REFRENCES

1 Lin, Qin; Ye, Wen; Yu, Zongsen. In: Proceeding of The Fourth National Application of RE in the Steel, 1992. 1.

2 Yu, Zongsen. Application of RE in the Steel, Beijing: Metallurgy Press, 1987. 238.

3 Hee, Kyun Park *et al.* Z. Metallkunde, 1982, 73 (H. 6): 399.

4 Yang, Zhiji; Liu, Woyuan. Iron and Steel, 1986, 21(4): 36.

5 Li, Daizhong; Gao, Shuqin; Zhang, Liefu *et al.* Journal of the Chinese Rare Earth Society, 1988, 6(1): 53.