QUANTITATIVE ANALYSIS OF TITANIUM, NIOBIUM, BORON AND VANADIUM PRECIPITATES IN STEELS

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Abstract - The morphology and crystal structure of Ti, Nb, B and V precipitates formed in micro-alloyed steels were investigated using scanning electron microscope(SEM), transmission electron microscope(TEM) and energy dispersive spectrometer(EDS), and their quantitative analysis was performed by inductively coupled plasma - atomic emission spectrometer(ICP-AES). The potentiostatic electrolysis method was successfully employed as an extraction method using 10% acetylacetone-methanol electrolyte.

Key words titanium, niobium, boron, vanadium, precipitate analysis

Recently, various kinds of micro-alloyed steels containing one or more of the elements such as Ti, Nb, B and V have been developed for the purpose of improving the mechanical properties. The quantification of the precipitates in micro-alloyed steels is essential to the understanding of metallurgical behavior and the development of new micro-alloying techniques[1-3]. The electrochemical extraction method is frequently applied to the extraction of precipitates like the compounds of carbide or nitride in steels[4]. In this work, the effectiveness of the potentiostatic electrolysis method[5-6] for extraction was examined, and its application to the quantification of precipitates was made.

EXPERIMENTAL

Apparatus Home-made potentiostatic analyzer, Jeol JEM-200CX STEM, Philips 515 SEM and Baird PS-4 ICP-AES were employed. The potentiostatic analyzer consists of 6 channel potentiostat, control system for each channel and three electrode cells[7].

Reagents The electrolytic solution was prepared by dissolving 10% of acetylacetone(AA, purity 99%) and 1% of tetra-methyl ammonium chloride(TMAC, purity 99%) in methanol(HPLC grade, purity 99.9%).

Specimen 10 kinds of steels (Table 1) were used for the precipitate analysis. Especially, samples H, I and J were prepared to investigate the change of precipitate amount with heat treatment.

TABLE 1. Chemical composition of various steels (unit:wt.%).

Sample	C	Mn	P	S	N	Ti	Nb	B	V
A	0.072	0.21	0.014	0.005	0.0022	0.003	-	0.0040	-
B	0.019	0.19	0.016	0.002	0.0010	0.001	-	0.0030	-
C	0.100	1.60	0.010	0.004	0.0040	-	0.0700	-	-
D	0.001	0.21	0.014	0.019	0.0016	0.063	-	-	0.0012
E	0.001	0.22	0.015	0.014	0.0022	0.004	0.0015	-	0.0250
F	0.003	0.15	0.012	0.008	N.D.*	0.045	-	N.D.	-
G	0.094	1.50	0.019	0.001	N.D.	0.016	0.0360	N.D.	0.0490
H	0.070	1.50	0.016	0.002	N.D.	-	0.0400	-	-
I	0.216	0.70	0.003	0.003	0.0013	0.050	-	0.0025	-
J	0.191	0.09	0.004	0.004	0.0185	0.025	-	0.0045	-

* N.D. = Not Determined

RESULTS AND DISCUSSION

[1] extraction of precipitates by potentiostatic electrolysis

Fig.1 shows the relationship between potential and current density. The left-side curve is for sample E, and the right-side curve for sample C. The curves for other samples are located between the curves for sample E and C. The shift of potential-current density curves to the left-side was observed for the samples of high carbon content. From Fig. 1, the potential of $-100 \sim 0$ mV and the current density of $60 \sim 100$ mA/cm² were selected for the extraction experiment. The selected potential was found to be effective for extraction and reasonable in extraction time. Generally, the amount of extracted precipitates increased observed as the carbon content increased.

Fig.1. Potential vs. current density curves for steel samples.

[2] SEM and TEM analysis (Table 2)

From the SEM analysis result, the precipitates of the A, B, C, G, H and J samples with high carbon content were observed to be cementite(Fe₃C). However, the coexistence of the precipitates of micro-alloying elements was confirmed in EDS spectra. In D, E and F samples with low carbon content, most of the precipitates were compounds of micro-alloying elements.

TABLE 2. SEM and TEM analysis results of precipitates.

sample	elements in ppt.*	ppt. type	size(μm)	shape
A	Fe, Mn	BN	0.01~0.1	round
B	Fe, Al, Mn, P, S	BN	0.01~0.2	round
C	Fe, Nb, Mn	Nb(CN)	0.005~0.02	square or round
D	Ti, Al, Mn, Fe, P, S	Ti(CN)	0.003~0.01	round
		FeTiP	0.02~0.2	square
		TiS	0.005~0.05	round
E	S, Al, Mn, Fe, P, Ti, V, Cu	CuS	0.02~0.08	round
		AlN	0.02~0.08	round
		MnS	0.3~0.6	round
F	Ti, S, Al, Cu, Fe, Mn	TiS	0.3~0.4	round
		TiMnS	0.1~0.3	round
H	Fe, Ti, Mn, V, Nb	TiNb(CN)	0.05~0.3	square
J	Fe, Cr, Ti, Mn, Al	Ti(CN)	0.01~0.05	square
		BN	0.03~0.1	round

* results of SEM EDS analysis.

In TEM analysis, the size, shape and type of precipitates were investigated. By electron diffraction pattern analysis, B and Nb were identified to exist in the form of BN and Nb(CN) type, respectively, while Ti was in various forms such as Ti(CN), TiS and TiMnS.

[3] chemical analysis

The quantification by ICP-AES was done for the precipitates extracted by the potentiostatic electrolysis. Analytical lines used in ICP-AES were Ti II 337.28nm, Nb II 316.34nm, B I 249.77nm, V II 292.40nm and Fe II 259.94nm. The detection limits of these lines were about 2~7ppb. The spectral interference of Fe on Ti, Nb, B and V lines was investigated because relatively large amount of Fe₃C existed in the precipitates for the samples with high carbon content. The calculation of spectral interference factor using Fe line intensity showed little effect of Fe interferences on Ti and Nb lines. However the calculated interference factors for B and V lines were 0.0042 and 0.00024, respectively. The Fe interferences on B and V lines were corrected for the calculation of B and V content in precipitates.

TABLE 3. The precipitate analysis results by ICP-AES for samples H, I and J with various heat treatment.

(a) Heat treatment of sample H

Sample	RT*	Rolling #1	Rolling #2	Holding Time	QR**
H-1	1250°Cx0.5hr	1000°C, 30%	900°C, 50%	-	WQ***
H-2	1250°Cx0.5hr	1000°C, 30%	900°C, 50%	-	Air Cooling
H-3	1250°Cx0.5hr	1000°C, 30%	900°C, 50%	-	Polymer Cooling
H-4	1250°Cx0.5hr	1000°C, 30%	900°C, 50%	10sec	WQ
H-5	1250°Cx0.5hr	1000°C, 30%	900°C, 50%	100sec	WQ
H-6	1250°Cx0.5hr	1000°C, 30%	900°C, 50%	1000sec	WQ
H-7	1250°Cx0.5hr	1000°C, 30%	900°C, 50%	1000sec	Air Cooling
H-8	1250°Cx0.5hr	1000°C, 30%	900°C, 50%	1000sec	Polymer Cooling

* RT ; Reheating Time, ** QR ; Quenching Rate, *** WQ ; Water Quenching

(b) Heat treatment of samples I and J

Sample	RT	CR*	Rolling Temp.	Holding Time	QR
I-1, J-1	1250°Cx4hr	-	1100~950°C	-	Air Cooling
I-2, J-2	1300°Cx3min	30°C/sec	-	830°Cx20sec	WQ
I-3, J-3	1200°Cx3min	30°C/sec	-	830°Cx20sec	WQ

* CR ; Cooling Rate

(c) Results of the precipitate analysis by ICP-AES

Sample	Elements as Precipitates(unit:wt.%)				extract. ppt.(g) (A)	calc.* ppt.(g) (B)	Δ ppt Wt.(g) (A)-(B)
	Ti	Nb	B	Fe			
H-1	-	0.0023	-	0.032	0.0015	0.0013	0.0002
H-2	-	0.0103	-	0.179	0.0034	0.0030	0.0004
H-3	-	0.0028	-	0.063	0.0017	0.0015	0.0002
H-4	-	0.0038	-	0.044	0.0015	0.0013	0.0002
H-5	-	0.0162	-	0.065	0.0019	0.0017	0.0002
H-6	-	0.0245	-	0.039	0.0019	0.0016	0.0003
H-7	-	0.0357	-	0.318	0.0049	0.0045	0.0004
H-8	-	0.0295	-	0.160	0.0031	0.0028	0.0003
I-1	0.0408	-	0.0004	0.533	0.0098	0.0094	0.0004
I-2	0.0173	-	-	0.029	0.0038	0.0031	0.0007
I-3	0.0123	-	-	0.066	0.0040	0.0035	0.0005
J-1	0.0215	-	0.0021	0.985	0.0167	0.0145	0.0022
J-2	0.0208	-	0.0014	0.031	0.0041	0.0027	0.0014
J-3	0.0220	-	0.0020	0.013	0.0036	0.0026	0.0010

* calculated ppt.(g) = [(extracted B + Nb + Ti + Fe (wt.%) + (total carbon (wt.%)]) x (dissolved sample wt.(g)) / 100

Table 3-(a) and (b) show the heat treatment procedures for samples H, I and J with different holding times and quenching rates. Table 3-(c) shows the precipitate analysis results for samples H, I and J. From this table, it was found that the amount of precipitates increased as the holding time increased and the quenching rate decreased. The change of precipitate amount with quenching methods was large for the samples without holding time, while it was small for the samples with 1000sec holding time. In the case of sample I-1, about 80% of total amount of Ti was precipitated because of the slow cooling rate (air cooling) although nitrogen content was low. But, in samples I-2 and I-3 compared with sample I-1, the amount of Ti precipitate decreased because of fast quenching rate (WQ) and low nitrogen content. In sample J-1 with high nitrogen content, Ti and B were mostly precipitated. Also, in samples J-2 and J-3, the amount of Ti and B precipitates was similar to sample J-1 due to high nitrogen content in spite of fast quenching rate.

The amount of precipitates was calculated on the assumption that all the precipitates exist in the carbide forms due to the negligible nitrogen content. Δ ppt, the difference between the extracted ppt and calculated ppt, can be explained by the amount of precipitates or inclusions from other elements except for Ti, Nb, B, V and Fe carbides. The amounts of extracted ppt and calculated ppt agreed well with each other for most samples. The exceptional large amount of Δ ppt can be explained by the presence of MnS and AlN precipitates. Therefore, the extraction method used in this experiment is considered to be reliable.

From Table 4, Ti and Nb formed the precipitates relatively well compared with B and V. In the case of sample C, for example, most of Nb (about 95%) existed in the form of Nb(CN) precipitate.

TABLE 4. The precipitate analysis results for the sample A-G.

Sample	Elements as Precipitates(unit:wt.%)					extract. ppt.(g) (A)	calc.* ppt.(g) (B)	Δ ppt Wt.(g) (A)-(B)
	Ti	Nb	B	V	Fe			
A	0.0023	-	0.0004	-	0.546	0.0055	0.0055	0.0000
B	-	-	0.0002	-	0.110	0.0014	0.0012	0.0002
C	-	0.0664	-	-	0.390	0.0076	0.0063	0.0013
D	0.0172	-	-	-	0.005	0.0004	0.0002	0.0002
E	0.0013	0.0014	-	0.0012	0.004	0.0008	0.0001	0.0007
F	0.0215	-	0.0002	-	0.007	0.0004	0.0003	0.0001
G	0.0118	0.0159	0.0003	0.0112	0.537	0.0072	0.0060	0.0012

* calculated ppt.(g) = [(extracted B + V + Nb + Ti + Fe (wt.%) + (total carbon (wt.%))] x (dissolved sample wt.(g)) / 100

CONCLUSION

Quantitative analysis of Ti, Nb, B and V precipitates in steels was performed by using home-made potentiostatic analyzer. The extraction time was significantly decreased by the independent control for each cell of the 6 channel potentiostatic analyzer. From the result of TEM analysis, we found that B and Nb existed in the form of BN and Nb(CN), respectively, and Ti existed in various forms such as Ti(CN), TiS and TiMnS. From the quantitative analysis by ICP-AES, we found that the amounts of extracted ppt and calculated ppt agreed well with each other. Therefore, we think that this analysis method is reliable.

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