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Energy-filtered EELS mappings of Copper Sulfide in steel involving a Trace Level of 0.01% Copper and its precipitated place

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A new concept [1-4] is reported that as small as 0.01% copper in steel plays as a sulfide-former and it stabilizes sulfur as copper sulfide (Cu-S) through TEM-based analysis of EDX and energy-filtered EELS elemental mappings.

Copper in industrially-produced blast-furnace & converter-based steel is too small to care the existence and the role at all. However, as small as 0.01% Cu is included as one of unavoidable impurities even if steel is categorized as high-purity. It has been believed that such a small amount of Cu exists as solid solution and has no effect on any precipitations in steel. Traditional ways of thinking are based on a viewpoint that sulfur in steel is stabilized as MnS by adding Mn and TiS and/or $Ti_4C_2S_2$ by adding Ti.

In this paper, we observe mainly through TEM-based analysis two kinds of ultra-low-carbon (0.001-0.002%) steel sheet samples including 0.01% Cu as an unavoidable impurity during steelmaking process to make clear the role of copper as a sulfide-former. Also the quantitative viewpoint is backed up by chemical analysis. As shown in Table 1, the samples are that a sulfide-former is only Mn in a first case (referred as ULC, Ultra Low Carbon steel) and Ti & Mn in a second case (referred as Ti-IF, Ti-stabilized Interstitial-free steel). ULC is as-hot-rolled sample and Ti-IF are both as-hot-rolled and as-annealed ones. TEM samples are prepared with 2-step extraction replica method.

The precipitation overview in ULC and the energy-filtered EELS elemental mappings are shown in Fig. 1 and 2, respectively. Although ULC has only 0.01% Cu as an unavoidable impurity, it is evident that Cu plays as a sulfide-former to make two shapes of Cu-S : (1)“Free-standing”-typed Cu-S and (2)“Coating”-typed Cu-S on MnS. Note that the sulfide at BN’s core is always “pure” MnS without any “Coating” Cu-S. As shown in Fig. 3, the quantity of precipitated sulfur as Cu-S occupies one-third of the whole sulfur. Also, Cu-involving precipitations in Ti-IF are also evident through Figs. 4 to 6. As shown in Fig. 4, sulfide in as-hot-rolled sample is mainly TiS and precipitates after annealing are changed into multi-phase-conjugated shapes : TiS is at the center, $Ti_4C_2S_2$ grows partially at and/or around the periphery of TiS, and Cu-S is observable at the overlapped area of TiS and $Ti_4C_2S_2$. The whole quantity of precipitated sulfur is the same in as-hot-rolled and as-annealed sample, but the percentage of each sulfide is changed : (1)Most of sulfide is TiS in as-hot-rolled sample, and (2)in as-annealed one $Ti_4C_2S_2$ and Cu-S increase, MnS gets slightly large, but TiS is reduced.

Cu-related sulfide precipitations are deduced through the microanalysis of ULC and Ti-IF. When only Mn is a sulfide-former (+0.01%Cu), it is presumed that Mn cannot stabilize the whole sulfur in steel and the rest of solute sulfur is precipitated as Cu-S by 0.01%Cu. Since Cu-S is not confirmable at MnS at BN’s core, it is estimated to be precipitated after BN is formed. When, in contrast, Ti is a sulfide-former, the whole solute sulfur is stabilized as TiS. It is deduced that TiS is changed into $Ti_4C_2S_2$ during annealing through the presumed reaction “$4TiS + 2[\text{solute C}] \rightarrow Ti_4C_2S_2 + 2[\text{solute S}]$” and that its re-solute sulfur is stabilized as Cu-S and MnS. The former is presumed to be precipitated more easily than the latter during steel sheet production process.

References

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[2] Y. Ishiguro, K. Sato and T. Murayama : Mater. Trans., 46, (2005), p. 769-778.
[3] Y. Ishiguro, T. Murayama et al. : Mech. Work. Steel Process., 35, (1997), pp. 255-264.
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Table 1 : Chemical Composition, Heat Condition and TEM-replica

sample	C	S	Mn	Ti	Cu	B	Heat process condition		2-step replica: supporting film	2-step replica: Mesh
ULC	0.0011	0.0073	0.17	–	0.01	0.0013	Hot-rolled	CT : 620 deg.C	Carbon	Ti
Ti-IF	0.0018	0.0074	0.15	0.040	0.01	–	Hot-rolled	CT : 680 deg.C	Al	Al
							Annealed	850deg.C		

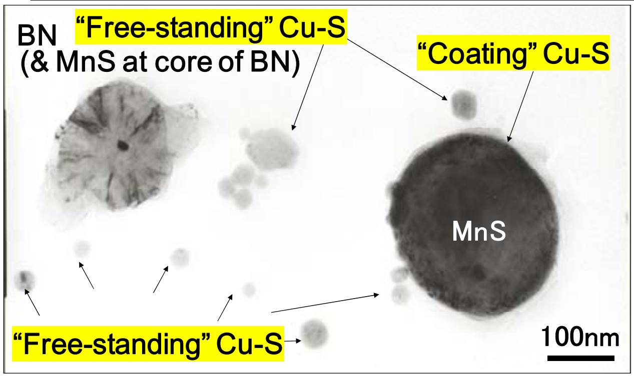


Fig. 1 : TEM micrograph of ULC sample

ULC
Sulfide-former:
Mn (+Cu)

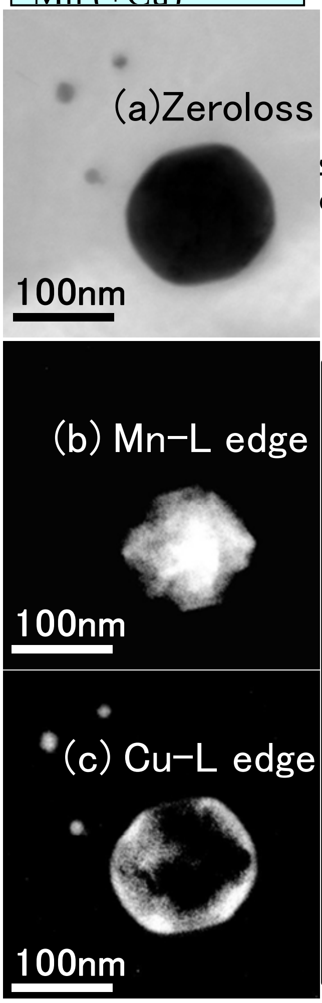


Fig. 2 : Energy-filtered EELS elemental mappings in ULC: (a)elastic, (b)Mn and (c)Cu

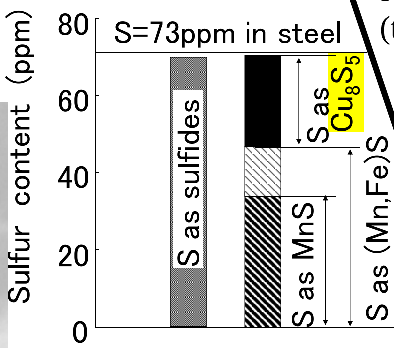
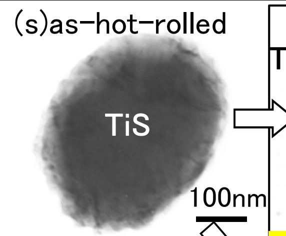


Fig. 3 : Quantitative chemical analysis of sulfides in ULC sample



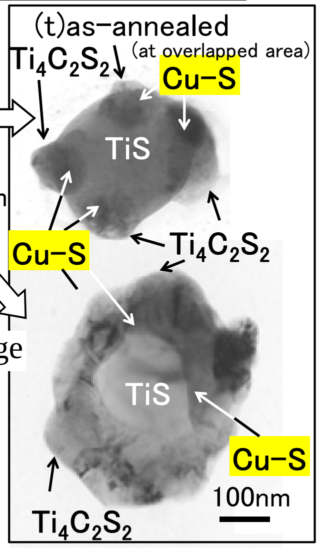
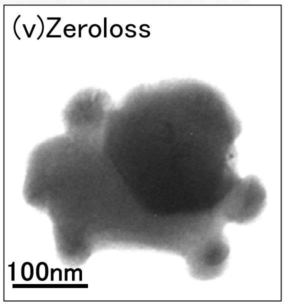
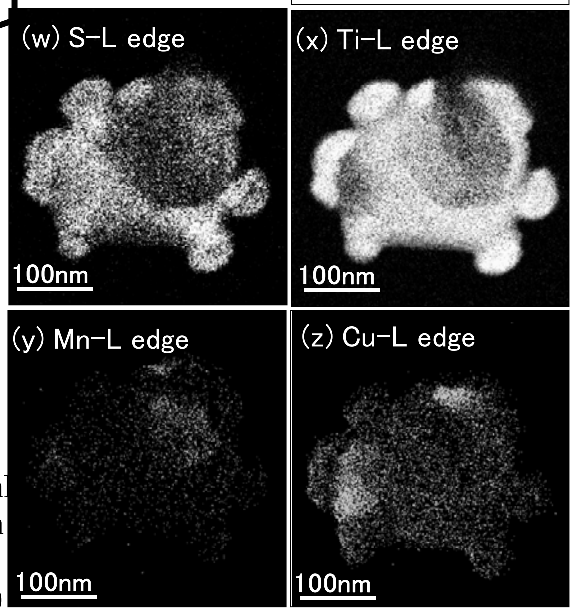


Fig. 4 : Morphological change of sulfide in Ti-IF sample : (s)as-hot & (t)as-annealed

Ti-IF
Sulfide-former:
Ti & Mn (+Cu)





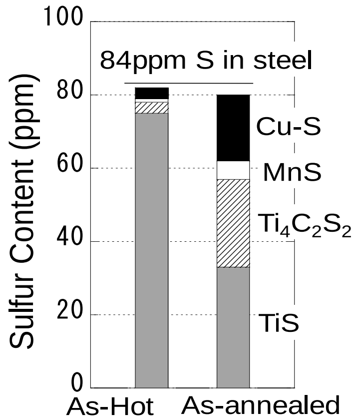


Fig. 6 : Quantitative chemical analysis of sulfides in Ti-IF sample (as-hot & as-annealed)

Fig. 5 : Energy-filtered EELS elemental mappings of multi-precipitate-conjugated sulfide in annealed Ti-IF : (v)elastic, (w)S, (x)Ti, (y)Mn & (z)Cu