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Solidification of Metals and Alloys,
Year 2000, Volume 2, Book No. 43
Krzepnięcie Metali i Stopów,
Rok 2000, Rocznik 2, Nr 43
PAN – Katowice PL ISSN 0208-9386

THE NITRIC-HYDROFLUORIC ACID ETCHING SLURRIES AS THE SLAG-FORMING AGENT FOR STEEL TEEMING

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1. Introduction

For peeling a surface of tubular billets from alloyed and high-alloyed steels in tube manufacture the acid etching in mixture of nitric and hydrofluoric acids are used. Such wasted etching solutions with acid content up to 6% are neutralized by lime milk with subsequent burying of forming sediments in special waste banks. Insufficient part of this slurries are used in cement manufacture, as pigment for brick making, for heat isolating materials. The chemical and ingredient composition and possible variants of such slurries using in metallurgy were studied.

2. Conditions of nitric-hydrofluoric etching slurries formation and their properties

By etching of tubular billet's metal from alloyed steels, the interaction between atom of iron, chromium and nickel and acid radical of take place that results of corresponding salts forming.

Neutralization of etching waste solution of limewash are proceeds at the expense of exchange reactions which results to forming calcium flourite, hydroxides of iron, nickel, chromium etc. and calcium nitrate (reaction without adjustment):

$$Me^{+n} + H^+ + F^- + NO_3^- + Ca^{2+} + (OH)^- + Ca(OH)_2 \rightarrow Me(OH)_n + CaF_2 + H_2O + CaNO_3$$

Table 1 presents thermodynamic characteristics, temperature of melting (boiling) and solubility of possible products of neutralization reaction.

Table 1. Physicochemical properties of possible products of neutralization reaction in waste solution of alloyed steel nitric-hydrofluoric etching

Chemical compound	$-\Delta H°_{298}$, kJ/mole	$-\Delta G°_{298}$, kJ/mole	Temperature of melting (boiling), °C	Solubility, g/100gr H_2O by 20°C
FeF_2	712	686	1100 (1837)	Insoluble
$Fe(OH)_3$	825	-	Decompose	Insoluble
$Fe(NO)_3 \cdot 9\ H_2O$	-		198 (Decompose)	83
NiF_2	658	636	1450 (1474)	Insoluble
$Ni(OH)_2 \cdot 0.25\ H_2O$	679	-	Decompose	Difficulty soluble
$Ni(NO)_3 \cdot 6\ H_2O$	428	-	237 (Decompose)	∞
CrF_2	679	755	1100 (1300)	Insoluble
CrF_3	-	-	1000 (Decompose)	-
$Cr(OH)_3 \cdot 2\ H_2O$	1035	-	Decompose	Insoluble
$Cr(NO)_3 \cdot 9\ H_2O$	-	-	38.5 (Decompose)	Freely soluble
CaF_2	1220	1200	1403 (2500)	Insoluble
$Ca(OH)_2$	987	-	Decompose	0.165
$Ca(NO_3)_2$	938	-	561 (Decompose)	129

As issued from this data the biggest part of forming (by neutralization of waste solution) compounds have the limited solubility in water and leave a sediments. The calcium nitrate left in solution.

The sediments of acid waste solution neutralization of sewage treatment installation of tube work in south of Ukraine were studied. The slurry after dewatering processing on filter press had following properties:

– colour – hell brown;
– aggregate condition– solid, in kind of plates;
– specific gravity (ton/m^3) – 1.25–1.42;
– humidity, % – up 40;
– chemical compound (in recalculation on oxides), % wt: SiO_2 – 1.0–2.0; CaO 25–30; CaF_2 – 15–20; Al_2O_3 – 7–10; Fe_2O_3 – 3–5; Cr_2O_3 – 1–5; NiO – 1–3; P_2O_5 1–3; S 0.03–0.06.

3. The method of nitric-hydrofluoric slurries processing

Analysis of ingredient compound displayed that metals (iron, chromium, nickel) presented in sediments in hydroxide kind and calcium is in kind of nitride and fluoride. By optimal regimes of roasting both the metals hydroxides and calcium nitrate decomposed with forming oxides of corresponding metals. Calcium fluoride left without change (melting temperature – 2510° C).

Thus, after roasting the thermal breakdown product consists of oxides of metals and calcium fluoride, which are valuable and critical materials in metallurgy.

For definition of optimal regimes of thermal break-down of acid etching slurries the thermal analysis were carried out. It has been established that temperature of decomposition beginning is 60-70°C so far as the water release (in that number from hydroxide compound). The temperature interval of decomposition completion was 690–720 °C.

The products of thermal break-down of slurries which taking by different regimes (roasting temperature 800–1300°C, oxidizing and reducing atmospheres) consist following compounds, wt %: SiO_2 – 2.0–4.0; CaO – 27.0–29.7; CaF_2 – 29.0–34.0; FeO + Fe_2O_3 – 0.1–10.7; Al_2O_3 – 3.0–20.9; MgO – 2.3–4.2; Cr_2O_3 – 2-6; NiO – 1–5; S – 0.01–0.06.

We can see that main components of products are CaO and CaF_2; materials basicity is 7–14; melting temperature – 950–1150°C; sulphur content is relatively low. Bulk densities of received materials are: roasted by 850°C – 1.09 ton/m^3, melted – 1.51 ton/m^3. Pycnometer density of melted material is 2.08 g/m^3.

Received physic-chemical properties of thermal breakdown products allow to recommend there as slag forming mixture for uphill teeming of killed steels.

4. Experimental tests of slurries as slag-forming agent by steel teeming

Experimental tests of thermal break-down product fi-om slurries by uphill teeming of killed steels were carried out in commercial conditions of converter foundry of Dzerginski Iron and Steel works (Dneprodzerginsk, Ukraine).

The steel mark 20 for tubular billet was cast in mould H1:1 with heat isolating plates. Expenditures of experimental material and compared slag-forming mixture "Ferrax" were 2 kg/t of steel.

Teeming temperature and duration of mould filling corresponds to technological demands. After stripper the part of experimental and compared ingots was lain on depository for surface examination. The rest of ingots were processed on tubular billets of 150-mm diameter. From billets (corresponding to head, middle and bottom parts of ingots) the samples for metal quality evaluation were cut.

Analysis of investigation results showed:

1. experimental material melts on 0.5–1.5 minutes quickly as compared mixture (2'–2' 20" from teeming beginning opposite 2' 30" – 2' 20");
2. experimental material is more agile on mirror of metal;
3. visual examination of ingots after stripper shown that compared ingots on 15–23% of height was covered by slag skin from non melted components of "Ferrax" mixture. Experimental ingots surface is clean and smooth, with less expressed (as compared) diametrical corrugation;
4. metallographic examination of metal macro and microstructure of experimental and compared ingots displayed:

– microstructure of metal both experimental and compared tubular billet is satisfactory and corresponds to OST M21-77 requests;
– in bottom part of compared metal the groups of enclosed slag are found. Whole, thequality of surface of experimental ingots was best.

The pilot taps of killed steels (1200 t) was cast with using of experimental material. The quality of rolled tubular billets that were cast with experimental material using instead "Ferrax" and satisfied to standards demands.

5. Conclusion

Thus, experimental testing showed that the material received by thermal break-down of slurries of neutralization of waste acid solutions of nitric-hydrofluoric etching is suitable to using as slag-forming agent by uphill teeming of killed steels.

Recenzował: dr hab. inż. Tadeusz Mikulczyński, prof. nadzw.

ABSTRACT

Results of investigation of compound and properties of slurries forming by acid etching of tube billets from alloyed steels was carried out. It has been shown suitability of thermal break-down product from slurries as slag forming agent to steel teeming.