Investigating the Melting Behavior of a CaO-MnO-SiO2-Al2O3 Flux for Use in Fusion Welding of Low Carbon Steel

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Abstract

CaF_2 has been commonly used as a constituent in oxide fluxes for welding of low carbon steel plates, owing to its strong ability to lower the liquidus temperature as well as viscosity of the molten flux. But, the adverse impact of fluorides on the health of the operating personnel and the environment has prompted a worldwide effort to replace CaF_2 with more benign constituents. The CaO-MnO-SiO_2-Al_2O_3 compositions, identified in the current work, have shown promise in terms of controlling oxygen transfer and inclusion generation in the molten metal, and can potentially be used as fluxes for welding of low carbon low alloy steels. However, the melting behaviour of the flux needs to be established before recommending its use. In addition to experimental measurements using High Temperature Microscopy (HTM) and Differential Thermal Analysis (DTA), and comparison with simulations from commercially available thermodynamic packages like FactSage™, this work also aims to understand the final composition and potential inclusions that could form in the weld pool using the selected CaO-MnO-SiO_2-Al_2O_3 flux.

1. INTRODUCTION

During fusion welding, the flux used needs remain molten till the weld pool has solidified. This implies that the liquidus of the flux should be below the solidus temperature of the weld metal. The molten flux should have adequate fluidity to quickly cover the molten metal and avoid aerial oxidation. Liquidus of fluxes used for welding of low carbon steel is usually maintained below 1400°C. In fusion welding processes, over the years, the harmful effect of the fluoride vapour emissions from the CaF_2 based fluxes, on the health and environment became increasingly apparent [1]. Hence the replacement of CaF_2 in the flux became a world-wide focus for researchers. But, CaF_2 has the ability to simultaneously reduce liquidus temperature, viscosity and oxygen potential which are essential during a welding process. Use of higher basicity slags containing multiple basic constituents, in order to optimise liquidus temperature, viscosity and reoxidation potential, has emerged as the most accepted approach in design and manufacture of welding fluxes. CaO, MnO, Al_2O_3 were the first popular choices for replacing CaF_2 in the welding fluxes [2]. Liquidus of fluxes used for welding of low carbon steel is usually maintained below 1400°C. A few compositions in the CaO-MnO-SiO_2-Al_2O_3 system, have shown promise in terms of controlling oxygen transfer and inclusion generation in the molten metal, and also have the predicted liquidus in the desired range for welding of low carbon low alloy steels. One such composition is analysed in the current work. However, the melting behaviour of the flux needs to be established before recommending its use. In addition to experimental measurements using High Temperature Microscopy (HTM) and Differential Thermal Analysis (DTA), and comparison with simulations from commercially available thermodynamic packages like FactSage™, this work also aims to understand the potential inclusions that could form using the CaO-MnO-SiO_2-Al_2O_3 fluxes by using the possibility of local equilibrium in a weld pool. Simultaneous use of multiple techniques is expected to enhance the reliability of the measurements [3].

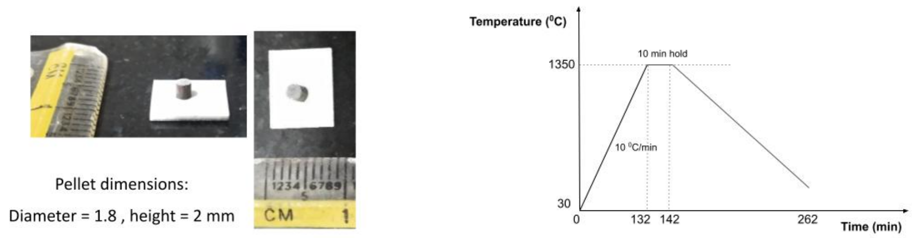
2. EXPERIMENTAL METHODS

2.1. Materials used

The flux mixture was prepared by mixing $CaO(40\%)$-$MnO(15\%)$-$SiO_2(39\%)$-$Al_2O_3(6\%)$ in the mentioned proportions. The materials used were purchased from Loba Chemie Pvt Ltd. Prior to mixing, CaO, Al_2O_3, SiO_2 powders were preheated to 1000 °C and MnO was preheated to 600 °C.

2.2. High Temperature Microscopy (HTM) measurements

High temperature microscopy is an image analysis system of a sample at preset temperatures, using a non-contact technique of heating and cooling. It is also used to analyse the sintering and softening behaviour of samples. A heating microscope of model HM 867, supplied by TA Instruments, was used for carrying out the experiments. The samples for the experiments were prepared using a die-punch set that comes along with the machine. The pellet has a diameter of 1.8 mm and height of 2 mm. These prepared pellets were placed on a small alumina ceramic plate (11 mm x 6 mm) for the experiments as shown in Fig. 1(a). All the measurements were carried out in air. The temperature profile set for the experiment is as shown in Fig. 1(b). Experiments were also repeated so that the results could be compared in a better manner. Images of the sample at the high temperatures were taken at regular intervals. Two pellet samples were made for the analysis.



(a) (b)

Fig. 1. (a) Sample prepared (b) Heating cycle for High Temperature Microscopy.

2.3 Thermal Analysis (DTA) measurements

Another method of determining the melting behaviour is by using the DTA or DSC method. In the current work DTA was carried out for the samples in air and the temperature profile is set as per Figure 1(b). A Netzsch™ STA 449 Jupiter unit, which could go to a maximum temperature of 1600˚C, was used for the measurement process.

2.4 FactSage^{TM} Weld pool composition analysis

One of the aims of using this particular flux composition is that apart from being an alternative to a CaF_2 based flux, it can probably also give inclusions in the weld which benefit toughness. To understand this, the Stream Equilib module in FactSage^{TM} software was used to analyse what would be the final weld composition at the welding temperatures. Although kinetics plays an important aspect in the final inclusions that will form in the weld, this method of equilibrium based analysis gives us an idea of the potential inclusions that could form. The base metal and electrode wire composition input was taken from the work of the authors [4], as the focus in [4] was also on welding low carbon steels. The composition of the flux being used in the current study was used as input along with the base metal and electrode wire composition. The calculations were done at 1600˚C.

3. RESULTS AND DISCUSSIONS

3.1. High Temperature Microscopy (HTM) observation

Fig. 2 shows the melting behaviour characteristics of sample 1 (S1) and sample 2 (S2) respectively at those temperatures at which the sample showed significant changes were reported. The sample S1, experiences a softening behaviour between 870˚C and 1277.9˚C. At 1301˚C and beyond the sample S1 is fully liquid indicating the liquidus temperature. However, sample S2 experiences a softening behaviour between 900˚C and 1305˚C. Beyond 1310˚C the S2 sample is completely liquid indicating liquidus temperature. But at 1267˚C for sample S1 and 1286˚C for sample S2, a significant rounding of the sample is observed, which is an indication for the solidus temperatures. This temperature difference of solidus and liquidus in the samples could be due to the inhomogeneity in the samples, as they are pre-mixed samples.

Observation	S1	S2
Rounding - start of softening (Solidus)	 1267 ^{0}C	 1286 ^{0}C
Meltdown - almost flat (Liquidus)	 1301 ^{0}C	 1310 ^{0}C

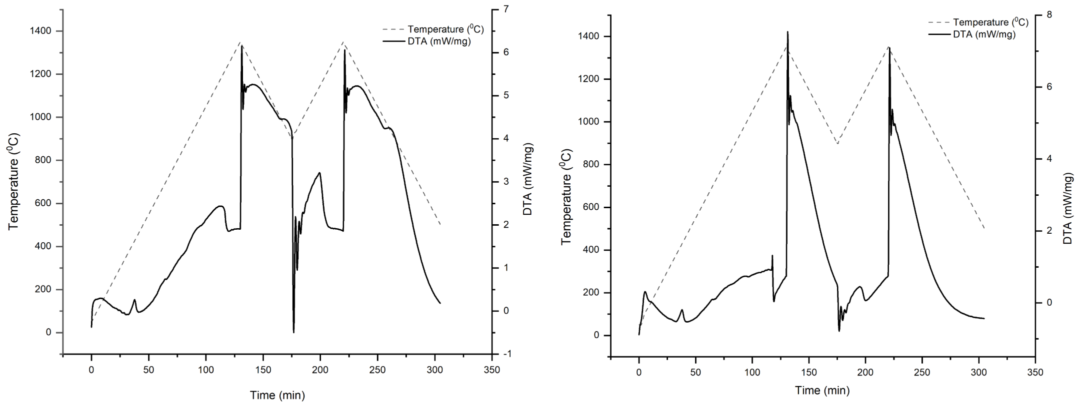
Fig. 2. Observations in HTM experiment

3.2. Thermal Analysis (DTA) observation

Fig 2. Shows the DTA of two samples from the as-mix flux mixture. There is a significant difference in the DTA signal in the first and second heating cycle. This is because during the first cycle the sample is still a solid and during the second cycle it has been melted (in liquid state due to the first heating cycle). This melting process will make the sample more homogeneous. Pre-melting of the sample was not done for the samples taken for the other experiment (HTM) hence, the values from the first cycle of the DTA are only considered for the solidus and liquidus temperature estimations. From the results observed as shown in Fig 2, it is understood that due to the nature of this experimental process, the liquidus estimation of the sample is more accurate. This is because the liquidus temperature represented by a downward exothermic peak is clearly distinguishable compared to the endothermic peaks corresponding to the solidus temperatures. Although the endothermic peaks are seen in few of the DTA plots, for uniform understanding here only the exothermic peak values are reported. Table I shows the exothermic peak values which indicate the liquidus temperature.

Table I. Observations from DTA plots

Sample	Exothermic Peak (liquidus estimation)
As-mix 1st batch (1b1)	1238.6 ˚C (Heat cycle 1)
	1179.6 ˚C (Heat cycle 2)
As-mix 1st batch (1b2)	1240.47 ˚C (Heat cycle 1)
	1148.51 ˚C (Heat cycle 2)



(a) (b)

Fig. 3. DTA plots of two samples from the as-mix flux (a) 1st sample (b) 2nd sample

3.3 Observations from FactSageTM weld pool composition analysis

In the FactSage^{TM} Stream equilib module, the three input compositions, which are the base plate, electrode wire and flux composition are equilibrated. The observations are reported in Table III. As per the obtained results Al_2O_3, SiO_2, CaO, FeO, MnO based inclusions could be formed on cooling in the weld pool as the slag liquid consists of them in significant fractions.

Table II. Observations from FactSage^{TM} Stream equilib module

Input (Temperature : 1600 $^\circ$C)									
wt%	C	O	Si	Mn	Al	P	S	Ti	Cu
Base plate (rest Fe)	0.12	0.007	0.155	1.340	0.067	0.019	0.007	0.005	0.030
Wire (rest Fe)	0.11	0.003	0.137	0.990	-	0.009	0.023	-	0.140
Flux	CaO-40		MnO-15		Al_2O_3 -6		SiO_2 -39		
Output	Fe Liquid 66.7 (C, Mn, Si, O are dissolved)		Slag Liquid 33.26 (Al_2O_3, SiO_2, CaO, FeO, MnO in significant fractions)						

4. CONCLUSIONS

The liquidus and solidus temperatures of the prepared fluxes were estimated. In the current work it is considered that the liquidus temperature estimation is from the DTA plots and solidus temperature from the HTM observations. It is due to the nature of the experiments. Table III shows the summary of the values from the experimental data and FactSage^{TM} analysis. The reason for these arbitrary observations could be the faster rate of acquisition of DTA data, due to which the exact liquidus point could have been missed. Also, as the shadow of the sample is captured in the process of HTM experiments, the first liquid could have formed earlier. In depth analysis is in progress. On the other hand, the FactSage^{TM} analysis shows that Al_2O_3, SiO_2, CaO, FeO, MnO based inclusions could form on cooling as the slag consists of them in significant fractions.

Table III. Summary of observations

Sample	Experimental Analysis		FactSage^{TM} analysis		Slag Atlas
	HTM	DTA			
	Solidus temperature estimation ($^\circ$C)	Liquidus temperature estimation ($^\circ$C)	Solidus temperature estimation ($^\circ$C)	Liquidus temperature estimation ($^\circ$C)	Liquidus temperature ($^\circ$C)
As-mix 1st batch	1267	1238.7	940	1306	~1300

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