

Oxy-hydrogen combustion and melt quality in secondary processes

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Aluminium production through secondary melting using recycled scrap, requires a fraction (5%-10%) of the energy required in the primary production route.

Combustion of conventional fuels (e.g., natural gas (NG)) in a reverberatory or a rotary furnace is a major source of carbon dioxide (CO₂) emissions.

Low-carbon intensity hydrogen (H₂) is being considered a key fuel in decarbonising these furnaces.

The use of hydrogen will affect the flame properties (e.g., no soot formation due to the absence of carbon in the fuel), emissions (NO_x), and furnace atmosphere, as no CO₂ is produced from hydrogen combustion.

The change in flame properties and the impact on the thermal efficiency and NO_x emissions can be addressed through specific burner designs.

The change in furnace atmosphere due to the switch from NG to H₂ can potentially impact aluminium melt and dross quality/quantity due to higher furnace water vapour (H₂O) and is an area of active study [1-2].

Application of oxy-fuel burners in secondary melting furnaces has demonstrated fuel efficiency gains as compared to cold air-fuel burners, reducing the NG fuel usage by up to 45% [3].

In gas-fired furnaces, the use of oxy-hydrogen burners has the potential to reduce the operational carbon footprint of melting furnaces.

However, it is important to ensure the use of oxy-hydrogen burners will not impact the process or the furnace.

Test Objective

In this study, the effect of changes in the furnace atmosphere, by switching the fuel from natural gas to hydrogen in oxy-fuel combustion, on melting characteristics of aluminium alloy 6061 is investigated.

Melt quality and oxide formation depend on several factors, including the material being melted (% Mg in the material, type of alloy), furnace and melt temperature, melt time, temperature-time history of the melting cycle, melt surface area exposed to the furnace atmosphere, flame type (burner

type and fuel or oxidisers used), and furnace atmosphere.

In this study, all these potential parameters that can impact the melt were kept similar across different experiments apart from the fuel type to investigate how a fuel composition change can impact aluminium melt and slag/dross properties.

Air Products' US Advanced Clean Energy Laboratory has a well-instrumented refractory-lined, custom-designed box research furnace for conducting batch melting experiments [4] and the study was executed in that test furnace (material placed in removable crucibles placed on the furnace floor).

Subsequent effects of fuel change on the amount and composition of dross formed in the dross layer were studied using X-ray diffraction (XRD) and Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS).

Experiment

This study used a pipe-in-pipe oxy-fuel burner to generate furnace atmosphere

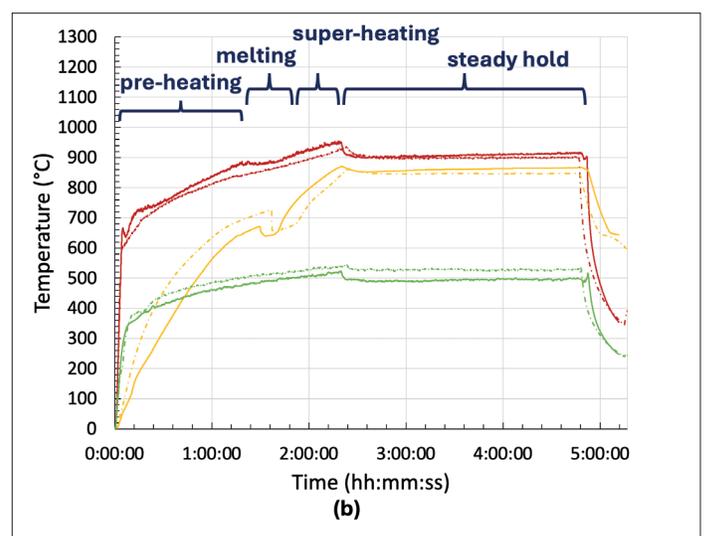
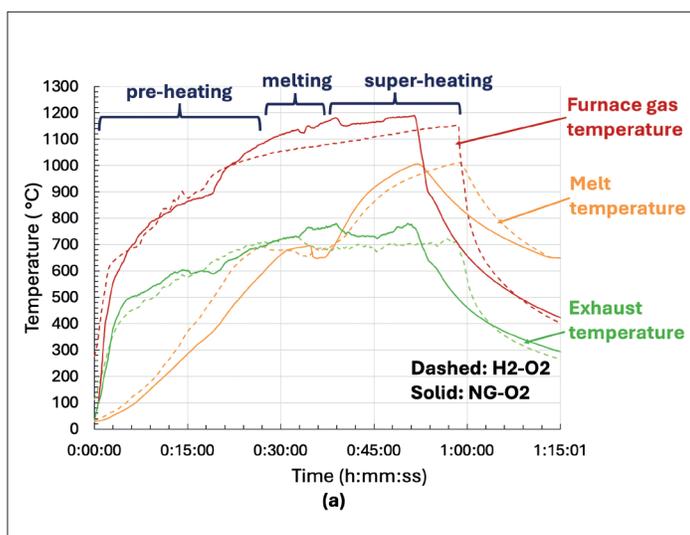


Fig 1. Comparison of key temperatures during the two melting tests. Short test (Left), Long test (Right)

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conditions (gas composition and temperature) similar to what is expected in an actual reverb or rotary furnace.

Air Products has developed a proprietary

smart Transient Heating Burner technology that can be used in reverb furnaces.

These burners are fuel-flexible (can operate with NG, H₂ or blends), and

produce lower emissions (NOx) compared to conventional oxy-fuel burners.

The combustion thermal power and the furnace gases (concentration of O₂, H₂O, and CO₂) are summarised in **Table 1**. The detailed experiment procedure and analysis process are described in [4].

Fig 1 shows a comparison of furnace, flue gas, and ‘inside crucible’ temperatures of the NG-O₂ and H₂-O₂ experiments.

Two studies were executed: a ‘short test’ that achieved melting and peak melt temperature of 1000 deg C and a ‘long test’ that had a hold time of 2.5 hours after melting at 850 deg C.

The temperature plots in Figure 1 show a similar temperature-time history for the two experiments, considering a variability of ± 50 °C in the measurement due to spatial distribution of heat and thermocouples position.

In the ‘Short Test’, the crucible temperature shows that the temperature increased first (measured gas temperature) and then dropped from about 700°C to 670°C as aluminium melting began.

The melted aluminium was further heated to 1,000°C before experiment shut-down and the furnace was purged with nitrogen to protect the melt from further oxidation by air that could enter the furnace from outside.

In the ‘Long Test’, after the melting, the melt was held at 850°C for 2.5 hours. The data is not suitable to study melt rate as it depends on several factors (flame type, burner design) and should be studied in an actual furnace.

Results and Discussion

Dross formation

The mass of the aluminium charge in each crucible was measured post-melting, where a net gain in its mass was noticed due to oxidation.

The results of weight change for the melts are summarised in **Table 2**.

The alloy shows similar level of oxidation for both NG and H₂ fuels in both the ‘Short Test’ and the ‘Long Test.’

Chemical composition analysis: slag/dross and melt

The results of the XRD analysis of the oxidised dross layer for the short test are shown in **Table 3**.

The two major phases present in the XRD spectrum are the MgO (periclase) and MgAl₂O₄ (spinel), which correspond to the makeup of the oxide dross layer formed over the melt.

The minor phases identified by the XRD analysis includes the silicate Mg₃Al₂(SiO₄)₃, the iron oxide (Fe₂O₃), and a titanium-chromium oxide (Ti_{0.1}Cr_{0.9}O₂) phase,

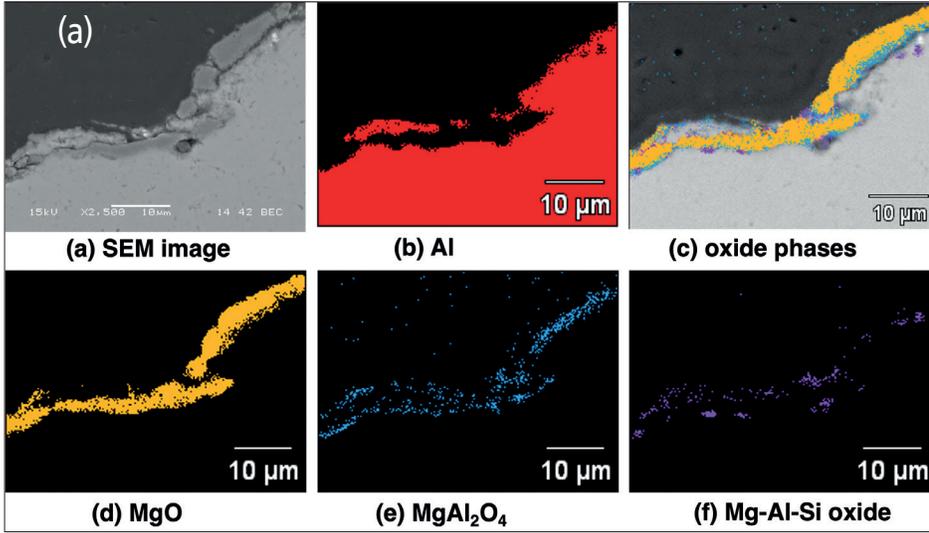
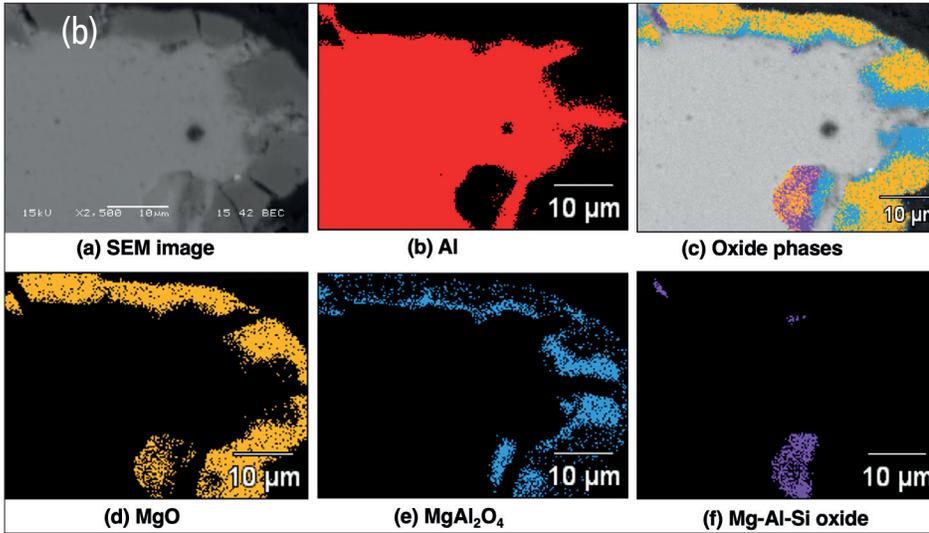


Fig 2. SEM image and phases present in the dross layer of the samples melted with a (a) NG-O₂ flame (b) H₂-O₂ flame.



Fuel/Oxidizer		NG/O ₂	H ₂ /O ₂
Thermal Power (Short Test)	MMBtu/hr		0.4
Thermal Power (Long Test)	MMBtu/hr	Melt: 0.16 and Hold: 0.12	
[O ₂] wet basis	Vol %	2.5 – 4.0	
[H ₂ O] wet basis	Vol %	60 - 65	95 - 97
[CO ₂] wet basis	Vol %	30 - 33	0

Table 1. Conditions inside the test furnace during melting operation.

		Short test		Long test	
		NG-O ₂	H ₂ -O ₂	NG-O ₂	H ₂ -O ₂
Net mass gain	Relative*	0.28%	0.14%	0.13%	0.15%

Table 2. The aluminium mass measurements before and after the melting (*initial mass of alloy: 7.21 lbs).

	MgO	MgAl ₂ O ₄	Al ₂ O ₃	Mg ₃ Al ₂ (SiO ₄) ₃	Fe ₂ O ₃	Ti _{0.1} Cr _{0.9} O ₂
NG-O ₂	x	x	-	x	x	-
H ₂ -O ₂	x	x	x	x	x	x

Table 3. Comparison of the compounds detected in the oxide layer of the NG-O₂ and H₂-O₂ melts during the short test (x: detected, - : not detected).

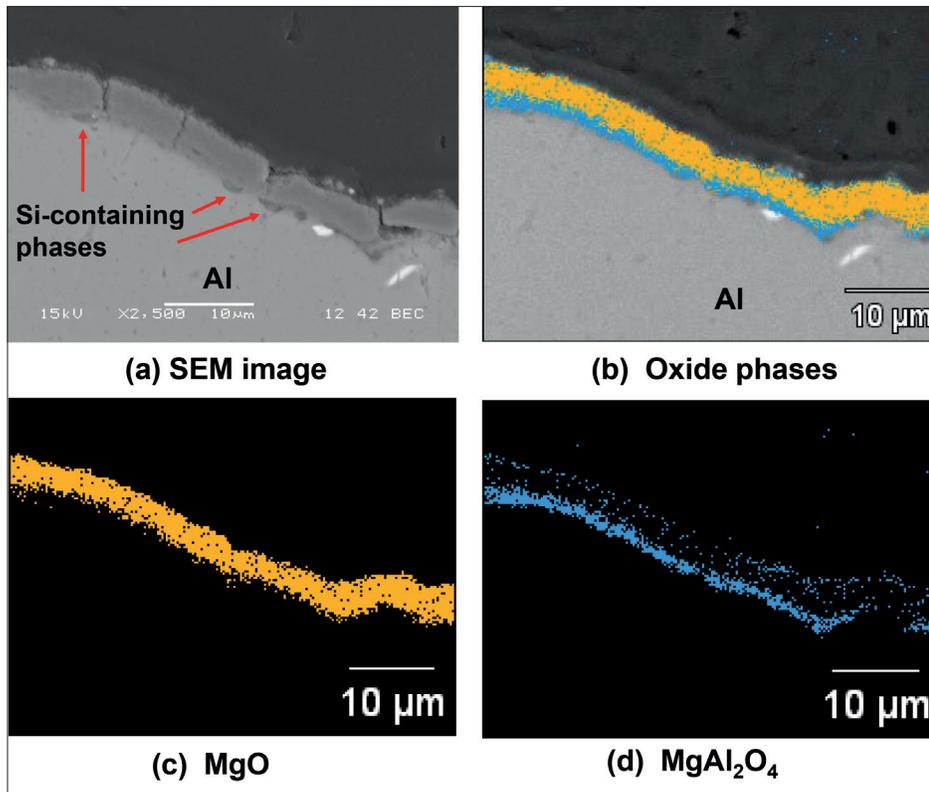


Fig 3. SEM image and major phases detected in the dross layer with SEM/EDS with H₂-O₂ flame.

corresponding to minor elements present in the alloy.

The results indicate the presence of alumina (Al₂O₃) in the sample melted with the oxy-hydrogen flame.

SEM/EDS Analysis

The surface samples of the solidified melts from the 'Short Test' were examined using an SEM/EDS to determine the morphology/elemental composition of the dross oxide layer. Details are covered in [4].

SEM/EDS images in Fig 2 show metallic aluminium in the core covered by a layer containing different compounds/oxides on the sample surface exposed to the furnace atmosphere.

The oxide consists of an MgO outer layer with MgAl₂O₄ present below the exposed surface. Other phases containing minor elements in the alloy are present below this surface, such as a silicon-containing phase as shown in image (f) of Fig 2 (a) and 2 (b).

The presence of both MgO and MgAl₂O₄ indicates that breakaway oxidation has started, but the fact that MgO is still detected shows the breakaway oxidation has progressed partially.

Comparison of Figs 2 (a) and (b) shows the structure and composition of the exposed oxide layer formed on the melt from both the NG-O₂ and H₂-O₂ flames are similar and consistent with the

pattern described above, an MgO-layer on the exposed surface with a more porous MgAl₂O₄ phase below the MgO layer.

Fig 2 (b) shows formation of an internal oxidation zone, below the top oxide layer, that contains MgO, MgAl₂O₄, and Mg-Al-Si oxides.

An aluminium layer separates the internal oxidation zone from the top oxide layer. In some areas of the melt from the H₂-O₂ flame, SEM/EDS maps show a relatively uniform 3-4 micron MgO layer covering the inner phases and the core aluminium phase (Fig 3).

This phenomenon could potentially protect the aluminium phase against further oxidation, reducing the melting losses.

Conclusions

The impact of changes to the furnace atmosphere from using hydrogen versus natural gas fuel (oxy-fuel combustion) on the 6061-aluminium melting and the melt properties was investigated in Air Products' Advanced Clean Energy Laboratory facilities.

Both melts (NG fuel and H₂ fuel) showed similar mass gains in the range of 0.14-0.28% of the initial charge.

The samples from the 'Short Test' were further analyzed and XRD patterns of slag powder samples from two melts indicated the presence of the two major oxides MgO (periclase) and MgAl₂O₄ (spinel).

SEM micrographs showed a dross layer (a few microns thick) over an internal aluminium core.

The dross layer consisted of an outermost MgO layer covering a more porous MgAl₂O₄ phase. Additionally, melt sample from the oxy-hydrogen flame indicate formation of a more uniform MgO layer protecting the melt from additional oxidation.

The experimental results from this study are encouraging for the use of oxy-hydrogen burners as a means to decarbonise secondary aluminium melting.

The total mass gain (dross formed) and type of oxides formed are similar between hydrogen and natural gas fuels for the 6061 alloy, demonstrating that melt yield was not adversely impacted with the fuel switch. Expanding the scope of future testing to include higher Mg-containing alloys will be needed for broader applicability across the secondary melting market.

It is important to note that while the high moisture content in the furnace atmosphere with hydrogen fuel did not result in additional oxidation of the melt pool, proper selection of the refractory material will be needed to understand effects on refractory life.

However, these initial results provide a strong basis for scaled-up testing in a reverberatory furnace and the continued evaluation of hydrogen as a viable fuel for secondary aluminium melting operations. ■

References

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