Gas/hydrogen blends as fuel to produce secondary aluminium

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Abstract

The research project 'Material Fundamentals Investigations for the Utilization of Renewable Hydrogen in the Production of Secondary Aluminum (01LJ2106A - C)' is funded by the Federal Ministry of Education and Research (BMBF). The 'KlimPro projects' supported by the BMBF focus on decarbonizing basic materials industries.
To investigate the influence of substituting hydrogen as a fuel on the quality of secondary aluminum, secondary aluminum samples will be melted with varying hydrogen enrichments, followed by subsequent material analysis.

Introduction

The global demand for aluminum continues to rise steadily. With its exceptional material properties, aluminum stands as an indispensable and forward-looking material with numerous applications. A notable characteristic distinguishing aluminum from many other materials is its ability to be recycled indefinitely without any loss of quality. Despite implemented measures such as air preheating, Oxy-Fuel technology, and modern MSR techniques, the production of secondary aluminum remains an energy-intensive process, predominantly reliant on fossil energy sources. The complete substitution of natural gas with hydrogen as a fuel could help to reduce CO2 emissions by 0.58 million tons of CO2 equivalent per year [1].
The hypothesis that the use of hydrogen as a substitute for natural gas could impact the quality of secondary aluminum is based on the observation that as the proportion of hydrogen in the fuel gas increases, the water vapor content in the exhaust gas also rises. The elevated water vapor content may lead to increased diffusion of atomic hydrogen into the melt. [2]

Experimental Method

Material

A remelted secondary alloy with 0.40 – 0.45 wt. % of Si and a Mg content of 0.45 – 0.5 wt. % was used in this work. The typical chemical compositions of the based alloy are presented in Table 1.

Table 1: Composition (%) of alloy that was used in experiments

alloy	Si	Mg	Fe	Cu	Mn	Cr	Zn	Ti	Al
AA6060	0.3 – 0.60	0.35 – 0.6	0.10 – 0.3	0.10	0.1	0.05	0.15	0.10	Rem.

Melting and Pouring

The melting experiments were conducted using the semi-industrial experimental furnace at the Gas- und Wärme-Institut Essen e. V. (GWI) in Essen. The experimental furnace is a construction of GWI, designed to expose material samples to various furnace atmospheres. The infrastructure for the melting experiments is illustrated in Figure 1. The central element of these experiments is the experimental furnace, equipped

with corresponding devices for exhaust gas analysis and temperature monitoring, as schematically shown in Figure 2 in cross-section. The desired furnace atmospheres and the required furnace temperature of 900 °C were generated using a standard BIC burner from Kromschröder (60 kW). Different fuel gas variations (from 100 % natural gas to 100 % hydrogen) can be controlled in the gas mixer using mass flow controllers. To ensure that no false air enters the furnace atmospheres, the furnace is maintained under positive pressure.

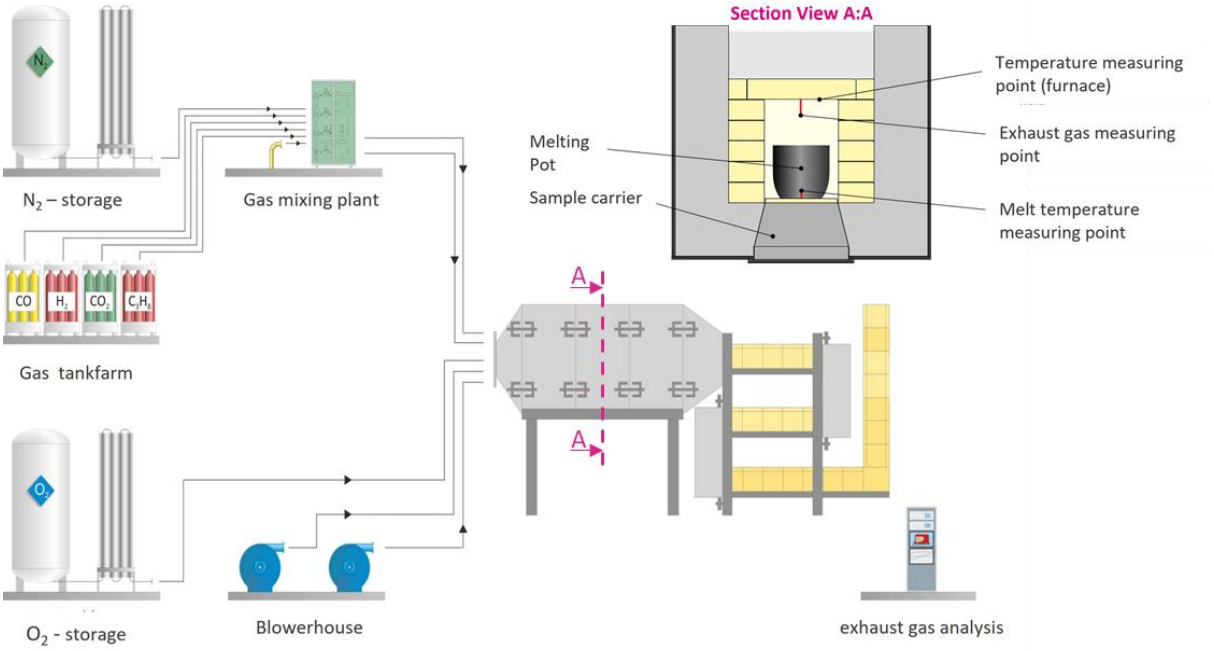


Figure 1: scheme of the experimental infrastructure (GWI)

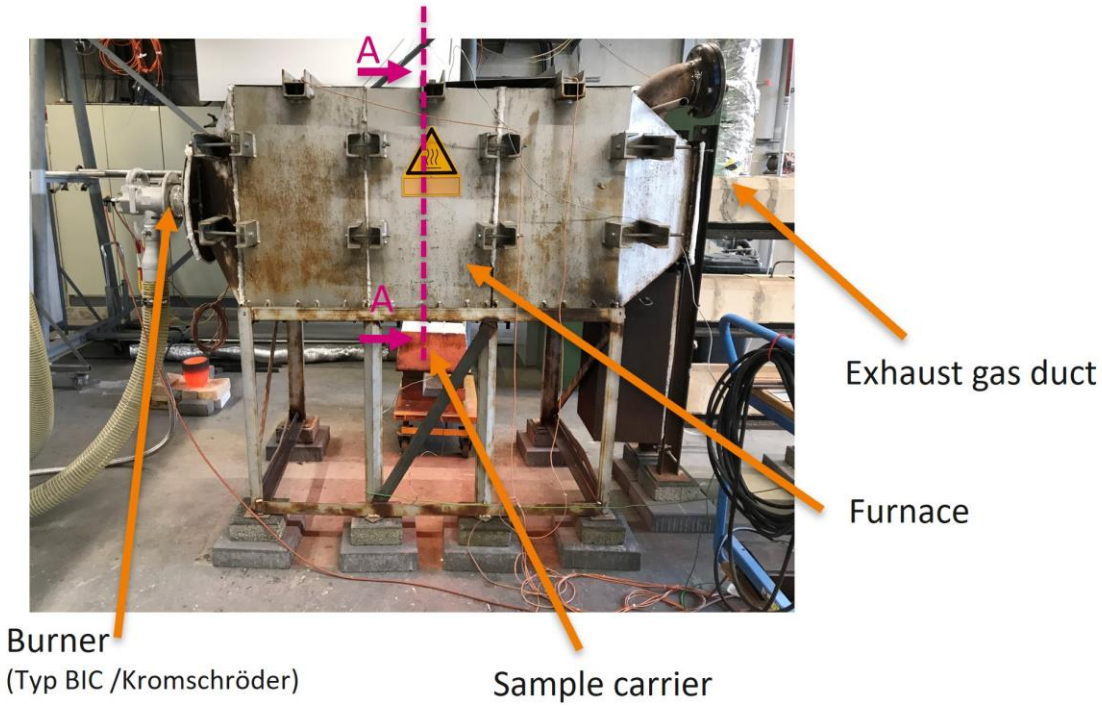


Figure 2: semi-industrial experimental furnace (GWI)

The temperature curve with holding times from the aluminium alloy melting tests is shown in Figure 3. The experiments resulting in a total melting time of around one hour including rebatching by reaching 780 °C melt temperature in liquid state for the first time. Whereby the melt in the pulpy or liquid state has a total contact time with the ambient atmosphere of around 45 minutes up to an extraction temperature of 780 °C.

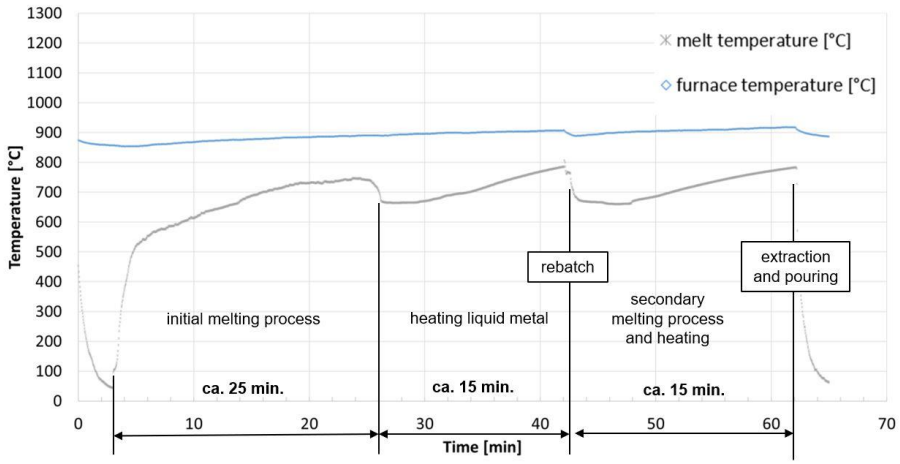


Figure 3: exemplary temperature curve of the casting experiments with 20 vol.-% hydrogen addition (OVGU)

The exhaust gas composition as a function of the set fuel gas compositions up to 100 vol.-% hydrogen are shown in Figure 3. It should be noted that a volume related admixture of up to 50 vol.-% hydrogen has almost no potential in reduction of the emission products CO_2. Only with an admixture rate above 50 vol.-% hydrogen there is a reduction in the greenhouse gas CO_2. It should also be noted that the NOx emissions in the tests carried out here are almost constant with increasing hydrogen content. But at 100 vol.-% hydrogen NO_x emissions rise very sharply (see Figure 4). The increase in NO_x emissions is mainly due to the formation of thermal NO due to higher adiabatic flame temperatures by the use of only hydrogen as fuel gas.

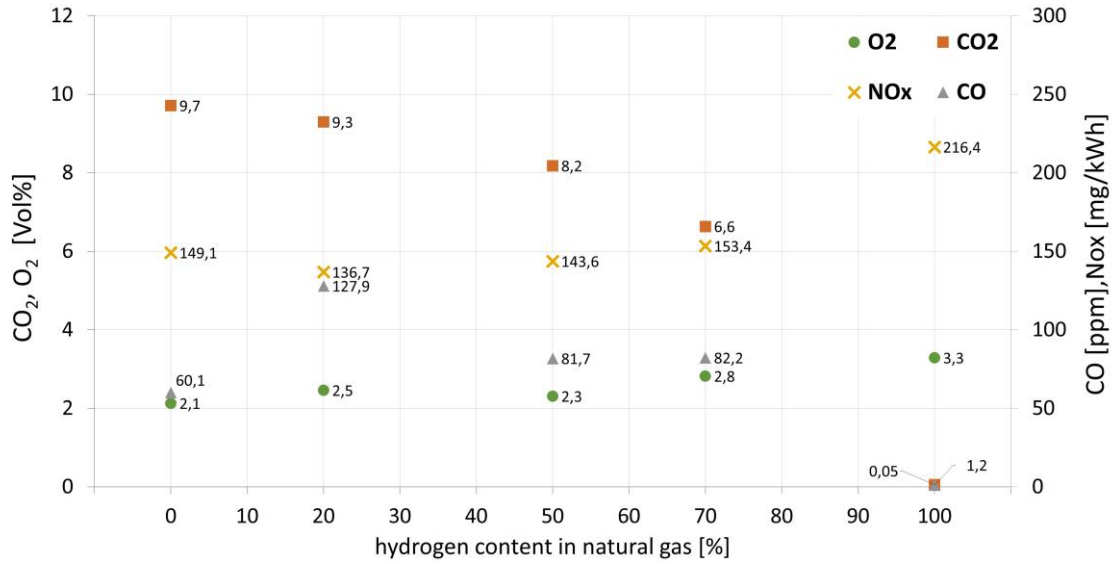


Figure 4: Averaged exhaust gas concentration during the tests (GWI)

The used die (refer to Fig. 5) was designed to fabricate 4 round test pieces each with a diameter of 20 mm and a height of 160 mm. Preheating of the mold was achieved through electrical heating cartridges, reaching temperatures up to 250 °C before each pouring. After extraction the designed crucible from the furnace at a temperature of 780 °C the melt was carefully skimmed to remove oxide layers from surface of the melt and was poured into the mold at 720 °C melt temperature. Each experimental was replicated three times, resulting in the pouring of three molds in each case and yielding a total of 12.

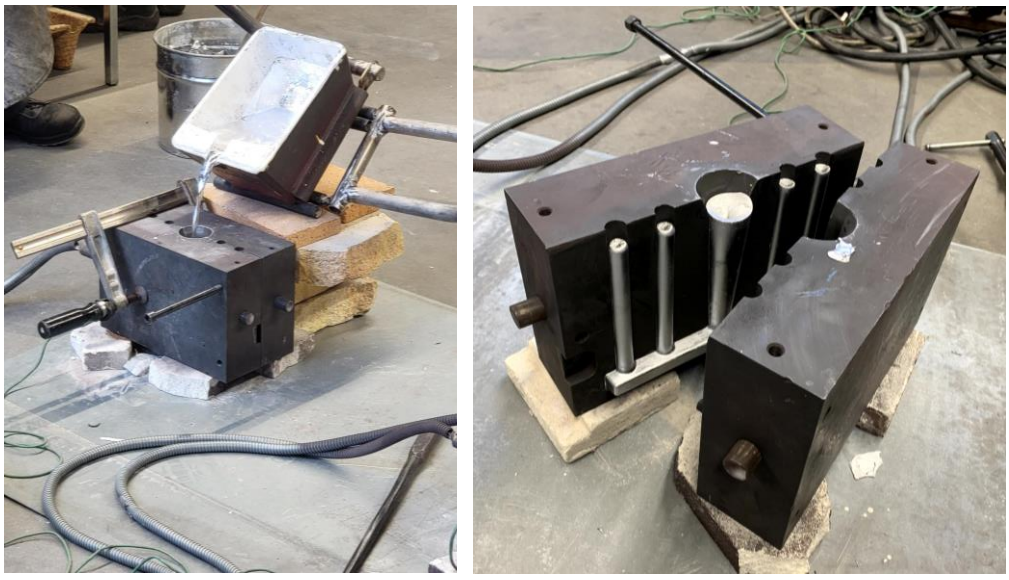


Figure 5: pouring the molten aluminium into the melt (left) and the resulting casting (right) (OVGU)

Analysis Methods

To determine the effect of hydrogen addition to the fuel gas on the melt quality, Al-Mg-Si alloys that had been melted at 900 °C were evaluated using a reduced pressure test (RPT). This test (also known as the Straube-Pfeiffer test), provides qualitative information of the overall uncleanness caused by the combined effects of inclusion content and hydrogen in the melt [3]. For the RPT, 100 g of alloy melt were cast and

solidified under one of two pressures: under atmospheric pressure in open air, or under a mild vacuum of 80 mbar. The densities (g/cm^3) of the two samples determined using Archimedes' principle, then the density index for the alloys was obtained as:

$$\boldsymbol{DI}\ [\%] = \frac{\boldsymbol{\rho_1 - \rho_2}}{\boldsymbol{\rho_1}} * \mathbf{100} \quad (1)$$

where ρ_1 is the density of the sample cast under atmospheric pressure, and ρ_2 is the density of the sample cast at 80 mbar.

For the quantification of area fraction of porosity, the whole cross section on the bottom of one test rod were obtained at a magnification of 200x. The porosity area of each specimen was estimated using a NIS Elements image analyzer. Subsequently round tensile specimens (DIN 50125-B6x30) were prepared and tested according to UNE-EN ISO 6892-1:2010 to determine the mechanical properties. Additionally, the round specimen were scanned by an XCT system, specifically the Nanotom from GE (refer to Fig. 6), with the X-ray source setup at 80kV and 160 µA. After acquisition and reconstruction of 600 XCT slices with a voxel size of about 20 µm, the sizes and volumes of defects/pores can be measured using an XCT slice process VG (Volume Graphic StudioMAX).

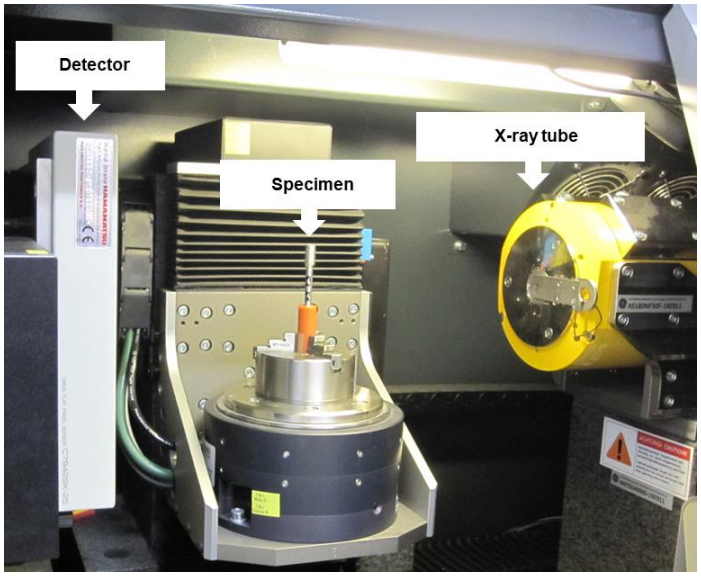


Figure 6: XCT system setup (OVGU)

Results: density index and porosity

Melt quality (Figure 7) of Al-Mg-Si alloys at 720 °C was estimated from hydrogen addition to fuel gas by using DI (density index) and pore analysis. DI after melting without a degassing process is at a high level independent of the fuel gas blend (DI = 18.00). Contrary to expectations, we obtained a slightly decrease in DI (DI = 16.18), for a 70 vol.-% hydrogen/ 30 vol.-% natural gas blend. The use of 100 % hydrogen to melt the secondary alloy the density index increased slightly (DI = 21.00). This unaffected melt quality by the fuel gas mixture may be a consequence of high initial hydrogen content of the melted secondary material, reduced diffusion rate because of the oxide layer and the hydrogen solubility limit of the alloy.

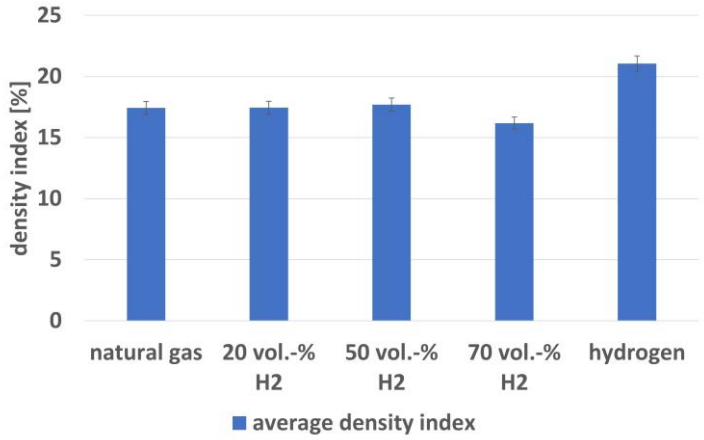


Figure 7: Density index (DI) of Al-Mg-Si alloys cast at 720 °C depending on the fuel gas mixture (OVGU)

The prepared samples from AA6060 secondary alloy were measured for porosity by microstructure image analysis as a sum of the defect area from the total cross section of the specimen with a diameter of 20 mm (Figure 8). The range of defect area values is from 0.029 mm² to 0.166 mm². In addition to the metallographic examinations, the volume porosity was determined by x-ray computer tomography. The highest volume porosity (0,53 %) was obtained when melting with natural gas. With the gradual addition of hydrogen to the fuel gas, the average volume porosity decreased. Generally, the obtained defect area and volume porosity (less than 0,6 %) are very small for a high density index of approximately 18 %. Further experiments further experiment are planned within the project to clarify the quantitative hydrogen content in the melt, role of the oxide layer for hydrogen absorption of the melt and resulting porosity.

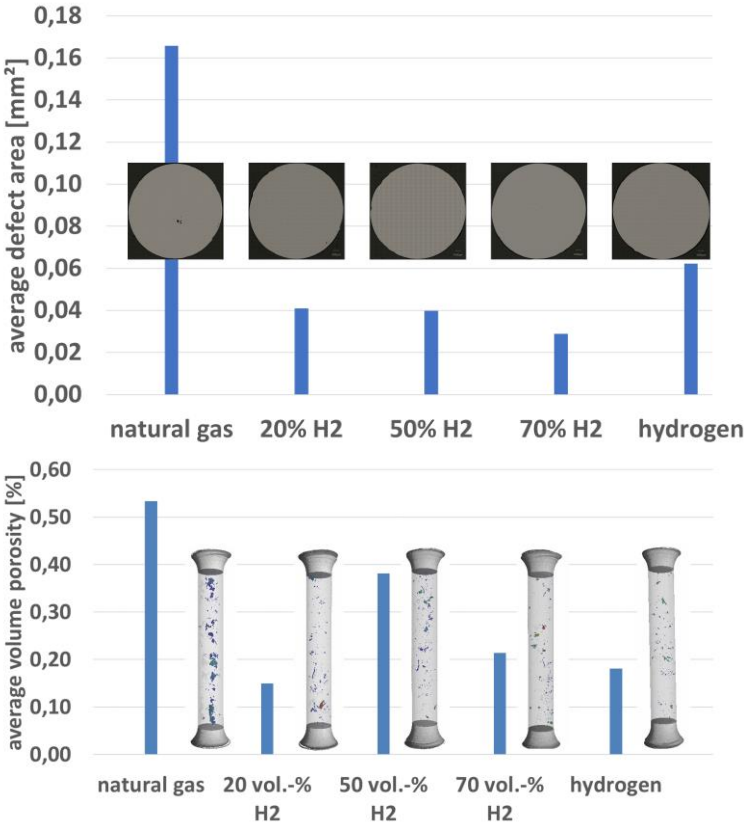
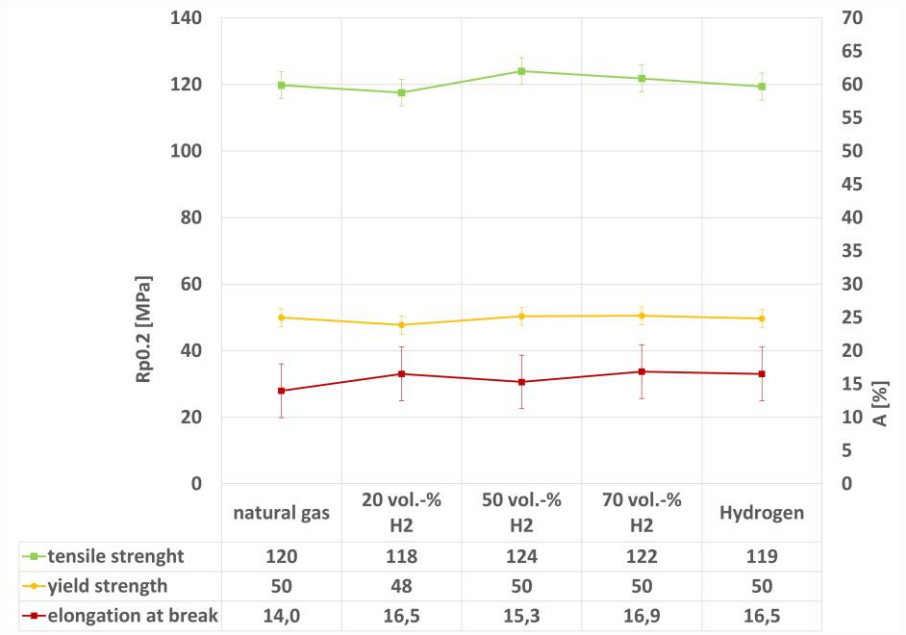


Figure 8: determined defect area in cross section (top) and volume porosity (bottom) (OVGU)

Results: mechanical properties

The yield strength was not changed by different fuel gas mixture, as seen in Figure 9. There is no significant difference between natural gas/hydrogen blends and an average of 50 MPa was observed for all casts. In addition, ultimate tensile strength (UTS) and elongation at fracture appear to have no difference either between the mixtures (Figure 9). The highest UTS was found with a 50 vol.-%/50 vol.-% blend of natural gas and hydrogen (124 MPa) and the lowest UTS was 118 MPa (20 % hydrogen), with a difference of 6 MPa. A 70 vol.-% hydrogen provided the highest elongation at fracture (16.9 %), while natural gas resulted in 14.0 %.



	natural gas	20 vol.-% H2	50 vol.-% H2	70 vol.-% H2	Hydrogen
tensile strenght	120	118	124	122	119
yield strength	50	48	50	50	50
elongation at break	14,0	16,5	15,3	16,9	16,5

Figure 9: obtained mechanical properties of secondary alloy AA6060 in state F (OVGU)

Conclusion

In this work, a secondary type AA6060 has been cast in test parts using gravity die casting. The impact of different natural gas / hydrogen blends, ranging up to 100 vol.-% hydrogen, on the melt quality (porosity and mechanical properties) in casting condition has been investigated. The following conclusions have been drawn:

- The density index when melting with natural gas is comparable to that with the hydrogen blends and slightly increases when using 100 vol.-% hydrogen.
- The assumption that porosity in the casting increases with the addition of hydrogen to the fuel gas did not prove to be correct. No significant influence or difference in the hydrogen blend on porosity was observed.
- There is no significant influence of the natural gas / hydrogen blends, up to 100 vol.-% hydrogen, on the mechanical properties (ultimate tensile strength, yield strength, elongation at fracture).

- Experiments are planned to investigate hydrogen absorption using a quantitative hydrogen measurement device over a holding period of several hours in different fuel gas mixtures.

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