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The influence of preheating gas chemistry on some properties of magnesia crucibles

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The quality of castings can be degraded if refractory material or reaction productions are picked up during alloy melting. This work shows that the chemistry of natural gas flames used to preheat magnesia crucibles can influence their reactivity when used to vacuum melt nickel base alloys. Preheating with a low oxygen, high temperature flame minimizes the calcia enrichment of binder phase material and formation of friable calcia–alumina melt/ceramic interfaces.

1. Introduction

Natural Gas is used to preheat magnesia crucibles used in the vacuum melting and casting of nickel base super alloy turbine blades. It is imperative that these components should be of the highest integrity and, therefore, the possibility of alloy/crucible interactions that could result in the entrapment of refractory inclusions is of concern. The programme described in this paper was undertaken to identify the preheating conditions that caused the least alloy/crucible interactions during subsequent vacuum melting. Full scale unselective foundry trials would have been wasteful, so the laboratory studies described below were conducted using magnesia crucibles obtained from several sources. In this work, crucible material was heated in natural gas flames using simulated foundry conditions. Care was taken to characterize the gas flames during this heating and evidence of structural and chemical changes produced by such heating was sought. In addition, the effects of gas heating on crucible performance, as defined by the wetting behaviour and chemical reactivity, were assessed.

2. Materials and methods

The ceramic used in this work was a magnesia crucible supplied by Refractory Mouldings and Castings Ltd. of Kegworth, UK, containing 3.0% Al_2O_3, 3.2% CaO, 2.8% SiO_2 and 0.6% Fe_2O_3 as binder material. This was heated using natural gas, CH_4 adulterated with 2.7% C_2H_6, 3.1% N_2, and 0.9% C_3H_8. After being heated some ceramic pieces were used as substrates for sessile drops of two nickel base alloys, whose compositions are given in Table I.

Small, 20 mm square, samples of the RMC crucible were placed in the bottom of another jacketted magnesia crucible and heated with a gas torch for 8 h. The natural gas/air mixture used to produce the flames were varied from run to run but kept constant during any one run. Flame condition was monitored primarily in terms of the oxygen level of the combustion products, measured using a Servomex OA 250 oxygen meter, and the gas mixtures were adjusted at the beginning of each run to produce a desired level. The carbon monoxide levels of the combustion products were measured using Draeger test tubes.

TABLE I Nickel base alloys used in the study

Alloy	Composition										
	Al	C	Co	Cr	Fe	Hf	Mn	Mo	Si	Ta	Ti	W
MSRR 7046	4.15	0.15	9.75	15.5	0.5	–	0.2	8.3	0.2	–	3.6	–
MSRR 7080	5.45	0.15	9.94	8.82	–	1.55	–	–	0.2	2.45	1.37	10.13

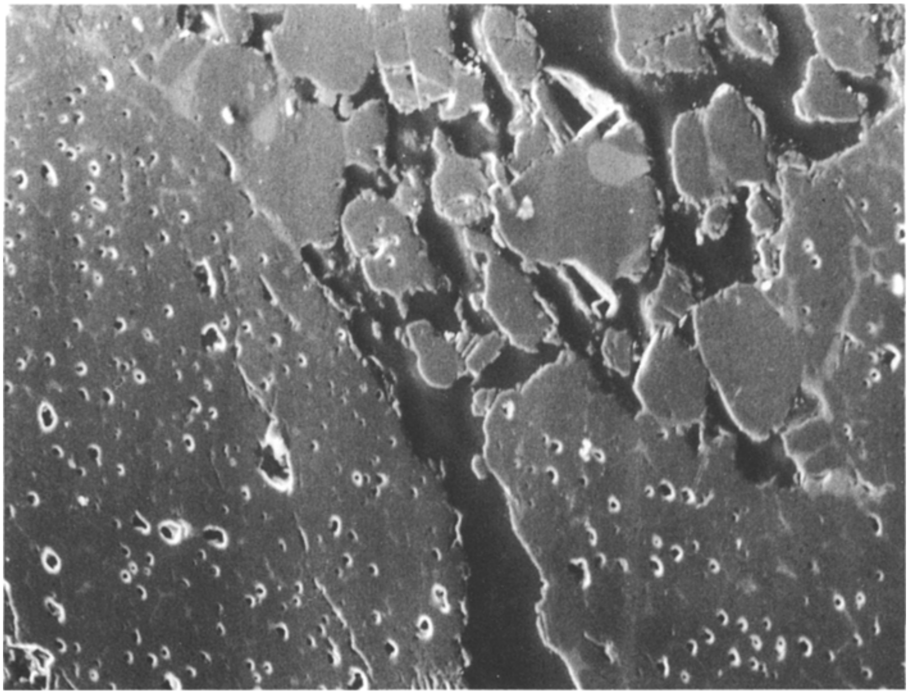

Figure 1 Scanning electron micrograph of unheated crucible materials, X 200.

The temperatures produced by the flames were monitored using a thermocouple buried in a dummy sample, and the flame appearance were recorded using colour photography. After such heating, the ceramics were used in sessile drop tests conducted in a chamber evacuated to 1 mPa. Small, 3 mm side, cubes of alloy were melted in ceramic substrates and heated to 1600° C for two minutes and then 1450° C for five minutes while their profiles were photographed. Gas desorption characteristics were assessed similarly by sampling the chamber atmosphere when rapidly transferred magnesia samples were reheated to 1500° C.

The effects of preheating and contact with molten alloys on the structure and chemistry of the ceramics were assesed using optical microscopy and electron probe microanalysis (EPMA).

3. Experimental results

3.1. Unheated crucibles

The crucible materials had very porous structures composed of large grains bounded by fine two phase regions, that appear as lighter patches in the scanning electron micrograph shown in Fig. 1. EPMA showed the grains to be magnesia containing traces of aluminium, calcium and silicon, yielding X-ray intensity ratios of 0.047 ± 0.004 for Al/Mg 0.052 ± 0.002 for Ca/Mg and 0.036 ± 0.007 for Si/Mg. The concentrations of the minor elements in the bonding regions were higher, the X-ray intensity ratios being 0.113 ± 0.033 for Al/Mg, 0.199 ± 0.011 for Ca/Mg and 0.110 ± 0.035 for Si/Mg.

When heated in a vacuum chamber, the ceramic desorbed small amounts of oxygen and carbon dioxide, while the contact angles derived from sessile drop profiles, Fig. 2, were 118° for MSRR 7080 and 108° for MSRR 7046. Optical examinations revealed little evidence of melt/ceramic interactions but EPMA surveys suggested that a 2 μm aluminium–calcium rich zone had been formed by the MSRR 7046 alloy.

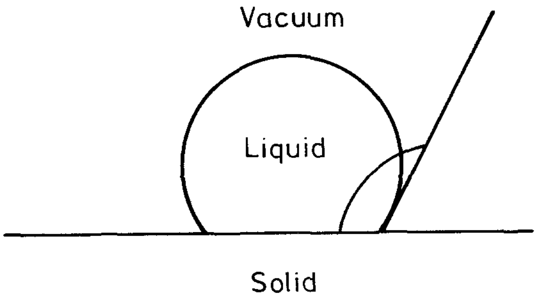

Figure 2 Sessile drop profile showing the contact angle. The least wetting liquid drops display the largest contact angles.

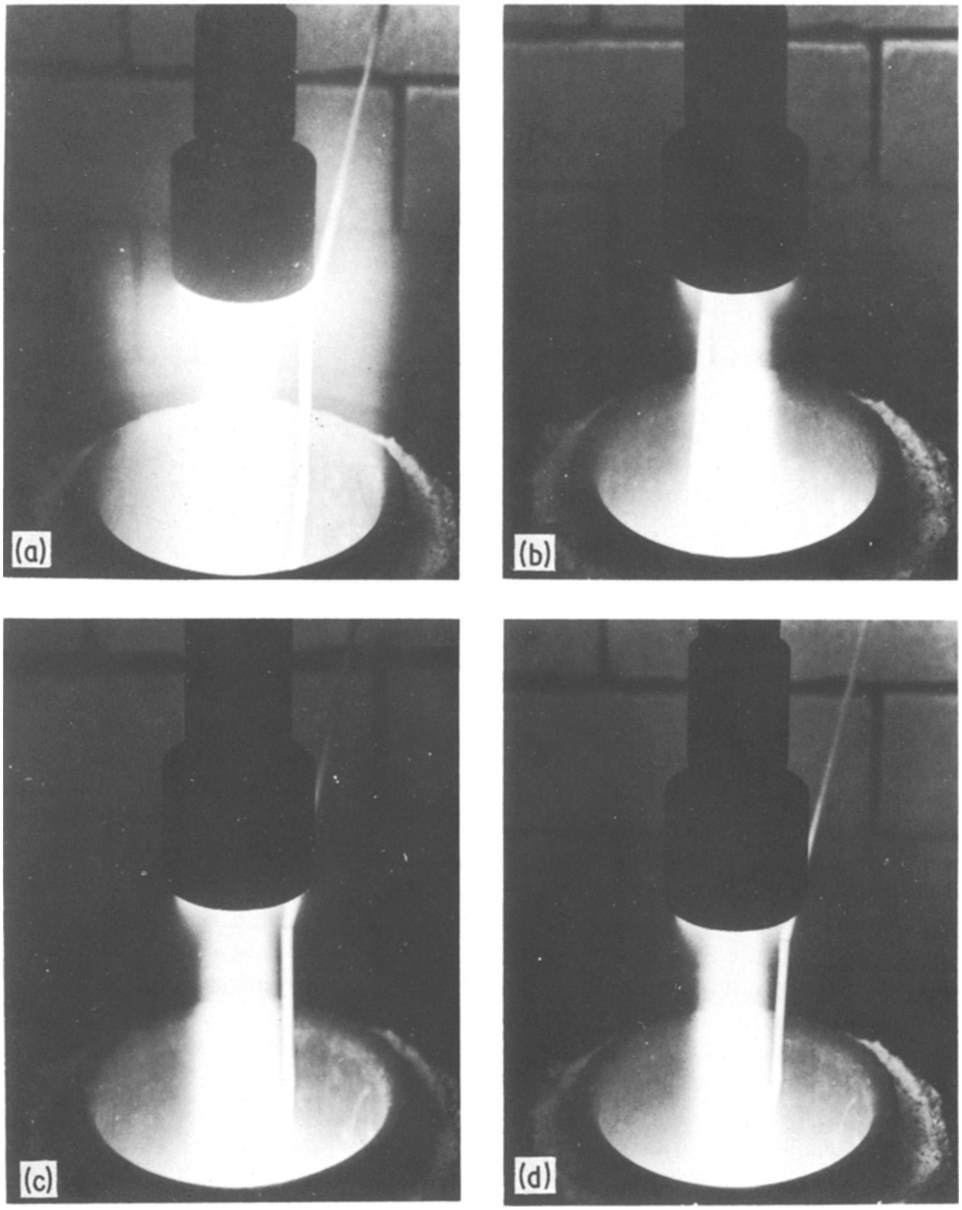

Figure 3 Flames whose combustion products have oxygen levels of (a) 0.1%, (b) 0.5%, (c) 1.1% and (d) 2.8%.

3.2. Effects of gas heating

Samples were heated in gas flames whose combustion products contained from 0.05 to 2.8% of oxygen. The low excess oxygen mixtures, containing 0.05 or 0.1% of oxygen in their combustion products, produced distinctive, blue, coronas such as that shown in Fig. 3 caused by the after burning of natural gas not consumed in the main flame. Changing the gas mixtures so that the oxygen contents of the combustion products increased caused accompanying decreases in their carbon monoxide levels and a fall in sample temperatures from about 1200 to 1100° C, Fig. 4. The heating also caused the sample weights to decrease by 0.02 to 0.04%, the greatest loss being produced by the low oxygen, hottest, flames.

Metallographic examination did not reveal any structural changes that could be attributed to the gas heating, but some compositional changes were suggested by EPMA surveys. Increasing the oxygen contents of the flames caused the aluminium, calcium and silicon contents of the large grains to decrease by 10 to 15% and those of the bond regions to increase by 50 to 200%. The Al/Si ratios

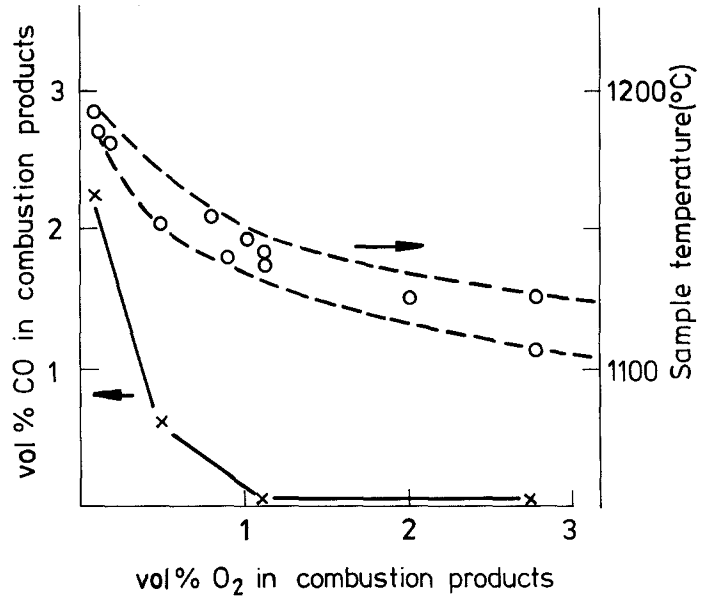

Figure 4 The relation of combustion product oxygen contents to the carbon monoxide levels and sample temperatures.

of the bond regions fell slightly but the Ca/Si ratios increased by about 45%, Table II.

Heating in vacuum caused the ceramics to desorb more carbon dioxide than the as-received ceramic and also some hydrogen, the proportion of which decreased from 11 to 0.4% as the oxygen content of the burnt gas increased from 0.05 to 2.8%. Sessile drop tests showed that flame chemistry, or temperature, affected the wettability of the ceramics, the contact angles assumed by drops of MSRR 7046 and MSRR 7080 decreasing as the oxygen contents of the flame combustion products increased to 1%, Fig. 5. No clear cut indications of alloy/ceramic interactions were revealed by optical microscopy but EPMA surveys of MSRR 7046/ceramic interfaces identified zones rich in aluminium and calcium that thickened from 2 to 20 μm as the oxygen contents of the flame combustion products increased from 0.05 to 2.8%. The thickest, 20 μm, zone had two equal layers that produced signals consistent with compositions of $3CaO \cdot Al_2O_3$ adjacent to the ceramic and SiO_2 contaminated $CaO \cdot Al_2O_3$ next to the alloy.

4. Discussion

This study has demonstrated that the chemistry of natural gas flames can affect the behaviour of magnesia crucible material and has characterized some of the effects. The material in the as-received condition was somewhat hydrated and it was not surprising, therefore, that the samples lost weight when they were heated or that the biggest losses should be caused by the hottest, lowest oxygen flames. While causing a weight loss, exposure to the burning gases also caused some of the burning gas to be adsorbed by the porous ceramic. The combustible species in natural gas are hydrocarbons which could oxidize to carbon dioxide

TABLE II The influence of preheating on grain and binder compositions

Heat treatment	X-ray signal ratios		
	Al/Mg	Ca/Mg	Si/Mg
Grain bodies			
0.05% oxygen	0.037 ± 0.009	0.060 ± 0.019	0.037 ± 0.010
0.45% oxygen	0.039 ± 0.013	0.054 ± 0.012	0.035 ± 0.009
0.95% oxygen	0.033 ± 0.012	0.057 ± 0.018	0.035 ± 0.009
2.80% oxygen	0.034 ± 0.011	0.048 ± 0.016	0.035 ± 0.010
Two phase binder region			
0.05% Oxygen	0.055 ± 0.003	0.102 ± 0.003	0.057 ± 0.004
0.45% oxygen	0.071 ± 0.003	0.181 ± 0.019	0.089 ± 0.009
0.95% oxygen	0.081 ± 0.006	0.179 ± 0.084	0.086 ± 0.037
2.80% oxygen	0.087 ± 0.070	0.305 ± 0.051	0.118 ± 0.038

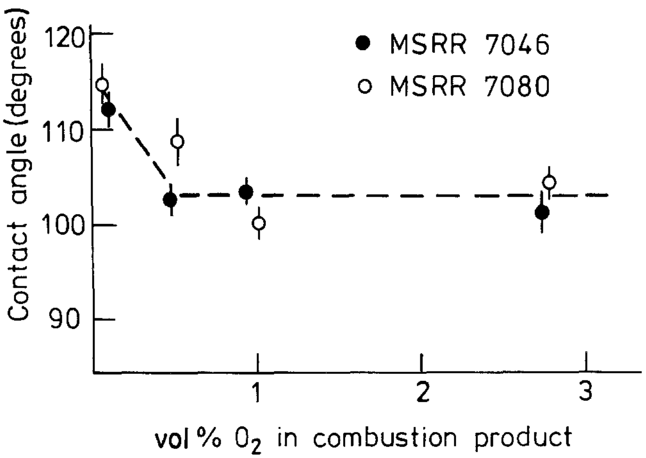

Figure 5 The influence of the chemistry of preheating flame combustion products and ceramic wettability.

and water. However, the gases desorbed from ceramic samples subsequently heated in a vacuum at 1500° C contained no trace of water, merely carbon dioxide and hydrogen, and we can but speculate that any adsorbed water may have been desorbed at lower temperatures or perhaps have been catalytically decomposed by the bonded magnesia surfaces to produce hydrogen. However, the fact that there was no great difference in the wettability of ceramic still warm from the gas heating or reheated after an overnight storage suggests that gas evolution effects are of minor importance in terms of crucible performance.

The primary factor that influenced the wetting behaviour and chemical reactivity of the magnesia samples was the chemistry, and hence temperature, of the gas flames. The changes in wetting behaviour shown in Fig. 5 were associated with an enrichment in the calcium, and aluminium and silicon, contents of the binder phases and a thickening of the calcia–alumina reaction zones formed at the melt/ceramic interfaces.

The consistency of these various observations permit some phenomological description. Thus the crucibles were sintered at very high temperatures, 1400 to 1700° C, so some binder phase material could dissolve in the magnesia and be retained in solution if post fabrication cooling rates are relatively fast. Reheating such a structure will cause an approach to equilibrium with transfer of excess components to the binder phase whose composition will change if they migrate at differing rates.

Some, but not all, of the information needed to access the validity of this description is available. Thus the solubilities of binder phase oxides in magnesia at 1500° C decrease in the order $CaO > Al_2O_3 > SiO_2$ [1–3] in accord with the X-ray signal intensities of magnesia grains in the as-received condition. Published data suggest low, invarient, solubility limits for Al_2O_3 and SiO_2 at temperatures below 1500° C, while extrapolation of CaO data suggest a progressive decrease from 1.1% at 1500° C to 0.2% at 1150° C. Solute redistribution motivated by supersaturation will require relatively rapid diffusion and this should be possible for calcium. Published data yield a diffusion coefficient of $3 \times 10^{-15}\,m^2\,sec^{-1}$ [4, 5] for Ca^{2+} in MgO single crystals at 1150° C which would permit a random walk migration of several microns during crucible preheating and much larger migrations, several millimetres, could be achieved by faster processes such as surface or grain boundary diffusion [6].

Thus this work has shown that changes in crucible wettability and reactivity characteristics can be caused by varying flame chemistry during preheating. The most effective gas heating is achieved by using a gas flame with the lowest possible excess oxygen content, and certainly less than 1%, which produces the least degradation of the non-wetting and chemical inertness characteristics of crucible materials. The results suggest that the degradation of these characteristics by high oxygen flames is due to their low temperatures which enhance the supersaturation of the magnesia and cause solute material, particularly calcium, to migrate to the binder phases and there react with molten alloys to form calcia–alumina compounds. Foundry practice now ensures that the excess oxygen contents of the preheating gas flames are minimized and hence possible refractory inclusion entrapment problems avoided [7].

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