INFLUENCE OF HAFNIUM ON THE WETTING CHARACTERISTICS OF MAR M-200

W. H. Sutton and D. R. Green

Special Metals
Member Company of Allegheny Ludlum Industries
New Hartford, New York

ABSTRACT

The sessile drop technique was used to study the effect of Hf additions on the tendency of MAR M-200 to wet Al_2O_3 . The reactions at and the microstructures of the interface between the solidified drop and Al_2O_3 were also investigated. The results showed that Hf promoted wetting by significantly lowering the contact angles, and that this lowering was not linearly related to the Hf content in the samples. The greatest decrease in contact angle occurred between samples containing 1.2% and 1.6% Hf, where a continuous, interfacial layer of HfO_2 was formed. The Hf in the melt reacted chemically with the Al_2O_3 substrate to form HfO_2 .

Introduction

The addition of Hf to both wrought⁽¹⁾ and cast^(2,3,4) superalloys has resulted in significant improvements in the ductility at room and elevated temperatures. Hafnium also modifies the melting and solidification behavior of the alloys. In MAR M-200, both the solidus and liquidus temperatures are lowered, and the temperature range between the two is increased⁽⁵⁾. During the solidification of nickel-base superalloys, the Hf partitions to the MC carbides, to the γ' phase, and also modifies the grain boundary structure of the heat-treated alloys^(2,3,4).

Hafnium also causes problems during the melting and casting of such alloys, because of its strong tendency to form oxides, carbides, and other compounds. Consequently, Hf-bearing superalloys are likely to chemically attack the crucible materials, thereby releasing unwanted elements and oxides (inclusions) into the melt. Unfortunately, HfO_2 is dense (density about 9.7 gm/cc) and thus cannot be removed by flotation.

This paper presents the results of a study on the effects of Hf in MAR M-200 on the wetting tendency of the alloy, and also on the chemical reactions which occur at the interface between the alloy and Al_2O_3 surfaces.

Experimental Procedure

Ingot slices of MAR M-200, containing from 0.46 to 1.95 weight percent Hf, were supplied by C. J. Burton from 15-pound laboratory heats (see ref. 5). Small cube samples, 6 mm on an edge and weighing about 1-gram, were cut from the slices and were melted on Al_2O_3 substrates to form sessile drops. The procedure was as follows: a sample cube of alloy was centered on a flat, high purity Al_2O_3 substrate (25 mm x 23 mm x 4 mm), which was then placed in a small vacuum furnace heated by a tungsten-mesh cylindrical element. The heating rate and the final temperature of $1500^\circ\text{C} \pm 5^\circ\text{C}$ was automatically programmed. A window in the furnace made it possible to photographically monitor the melting of the drop and to document the drop shape and contact angle. A liquid-nitrogen trapped, 4"-diffusion pump backed by a 1.6 liter/min. mechanical pump maintained a furnace chamber pressure of 10^{-6} torr (10^{-3} microns, μ) at the test temperature 1500°C (2732°F). After the drop had remained molten for 40 minutes, the power was shut off and the drop would then solidify within a few seconds. The solidified drops and sections through the drops and substrate were then examined under optical and electron scanning microscopes.

Results

The melting sequence of a sample cube on an Al_2O_3 substrate is shown in Figure 1. The contact angle, θ , which is reproducible to $\pm 2^\circ$, is shown in Figure 1C, and provides a direct measure of the alloy's wetting characteristics. For contact angles above 90° (i.e., Fig. 1B, $\theta = 108^\circ$) a non-wetting condition exists; for angles below 90° (i.e., Fig. 1C, $\theta = 62^\circ$) wetting occurs.

During the first 1-2 minutes after the drops had become molten, the contact angles fell rapidly for all compositions including that of the base alloy, as shown in Figure 2. This means that initially, the drops rapidly spread out over the surface of the Al_2O_3 substrates. In 5 to 10 minutes the spreading ceased, and the contact angles remained constant for the duration of the test. However, the final contact angles were dependent upon the amount of Hf in the sample. The effect of Hf on the contact angles can be seen more clearly in Figure 3, where a slight decrease in θ occurred between 0% and 1.2% Hf. A sudden 18° decrease in θ occurred between 1.2% and 1.6% Hf, and then θ remained constant between 1.6% and 1.95% Hf.

Figure 1: melting sequence of a Sample Cube of MAR M-200 plus 1.6% Hf at 1500°C, 10^{-3} micron pressure; (A) onset at melting, (B) complete melting (time = 0 min.), (C) after 30 minutes. The substrate is Al_2O_3 .

The effect of Hf on contact angles, along with some other melting data are summarized in Table I.

The surface discoloration of the Al_2O_3 under the molten drops and the effects of Hf can be seen in Figure 4. The base alloy sample shows a gray vapor deposit on the Al_2O_3 surface outside the drop (Fig. 4A) which is not seen in the Hf-bearing samples. The weight loss for all samples was approximately the same (Table I). In Figure 4B and 4C, the initial location of the cube sample can be seen as a square cross-sectional zone on the Al_2O_3 surface for the samples containing 1.2% and 1.6% Hf. This zone could also be detected in the 1.42% Hf sample, but not in the one containing 0.46% Hf. For the sample containing 1.95% Hf, this zone is barely discernible, and is partly obscured by the fact that the drop moved to the lower right-hand corner during the course of the test (Fig. 4D). For future reference, three distinct regions will be discussed:

1. Zone 1 - The region where the cube sample was originally located on the Al_2O_3 surface.
2. Zone 2 - The region under the molten drop, but which excludes Zone 1.
3. Zone 3 - The region on the surface of the Al_2O_3 which is outside of the drop.

Zones 1 and 2 on the matching contact surfaces of the drop bottom were also clearly visible for the 1.2%, 1.4% and 1.6% Hf containing samples.

TABLE I. Effect of Hf on the Wetting and Melting Characteristics of MAR M-200

Run No.	% Hf	Solidus (°C)*	Liquidus (°C)*	ΔT (°C)*	Carbide Soln. (°C)*	Contact Angle at 1500°C			Drop Weight Loss (%)
						0-Time	10-Min.	30-Min.	
243	0.01**	1315	1393	78	1332	104	90	90	13.5
245	0.46	1304	1386	82	1327	108	85	84	13.5
246	1.27	1290	1378	88	1319	106	80	80	13.0
248	1.42	1290	1378	88	1324	108	70	68	13.9
247	1.62	1290	1378	88	1321	108	62	62	13.9
244	1.95	1290	1378	80	1319	109	62	62	14.0

* - Reference 5

** - Base alloy composition = 9.2 Cr, 10.1 Co, 12.1 W, 1.0 Cb, 1.9 Ti, 5.0 Al, 0.1 C, 0.015 B, 60.6 Ni (in text, referred to as 0% Hf). The Al_2O_3 substrate was a fine grained, dense, 99.7% Al_2O_3 , supplied by National Ceramic Products Co.

Figure 2: Contact Angle vs. Time for MAR M-200 Containing Various Levels of Hf.

Figure 3: Effect of Hf Content on the Contact Angle of MAR M-200.

Figure 4: Photos Showing Discoloration of Al_2O_3 Surfaces Under Sessile Drops Containing Various Levels of Hf. The solidified drops separated from the Al_2O_3 during cooling and were moved aside to show the views above.

The matching surfaces of the drop bottoms and Al_2O_3 substrates were observed under the scanning electron microscope, which also had energy and wave-length dispersive capabilities. Figure 5A and 5C show the surface under the base alloy drop, while Figure 5B and 5D show the surface of the Al_2O_3 substrate. The drop bottom of the base alloy (no Hf) essentially replicates the surface of the Al_2O_3 grains. Embedded in the surface of this drop are darker particles, rich in W, Cb, and Ti, which are presumably carbides. No Hf was detected in either surface. Figure 5C and 5D show similar views, but of the sample containing 1.2% Hf. The Al_2O_3 substrate in this sample is covered with a nearly continuous network of HfO_2 grains (Fig. 5D), whose imprints can be seen on the drop bottom (Fig. 5C). Also, several particles can be seen protruding from the drop bottom, which are rich in W, Cb, Ti and some Hf (presumably carbide particles). Very little HfO_2 was attached to the drop base in Zone 1 or 2; most of the HfO_2 remained on the Al_2O_3 surface.

The bottom surface of the drop containing 1.6% Hf is shown in Figure 6. The Hf map (Fig. 6A) shows that unlike the 1.2% Hf sample, there is a heavy concentration of Hf in Zone 1, which is due to the attached HfO_2 oxide layer (Fig. 6B,C). Hafnium and oxygen maps were made of several other areas similar to that shown in Figure 6B, and the results indicate that the Hf is in the form of an oxide. The surface of the exposed alloy is shown in Figure 6D, where no protruding particles (carbides) can be seen (see Fig. 5C). In Zone 2 (Fig. 6A), there is some Hf, but this is a result of scattered patches of HfO_2 adhering to the surface (see lower half of Fig. 6B).

In Figure 7, the matching surface of the Al_2O_3 substrate under Zones 1 and 2 is shown. In addition, Zone 3 is shown in this figure. In contrast to the

Figure 5: SEM Views of the Contact Surfaces Between the Sessile Drop Bottom and the Al_2O_3 Substrate in Zone 1 for Samples Containing No Hf and 1.2% Hf.

drop surface in Zone 1 (Fig. 6A) there is relatively little Hf (except for scattered HfO_2 patches) on the Al_2O_3 surface (Fig. 7A). In Zone 2 on the Al_2O_3 surface, most of the Hf exists as a continuous HfO_2 layer (Fig. 7B), except for a few small patches which remain attached to the drop (Fig. 7A). In comparing Figure 7C with Figure 7D, it can be seen that the exposed Al_2O_3 grains, which were in contact with the Hf in the melt, are pitted and have been chemically attacked.

Discussion

Hafnium additions to MAR M-200 promote wetting by decreasing the contact angle on Al_2O_3 substrates, although they do not change the initial tendency of the base alloy drops to spread out rapidly during the first two minutes after their formation. The contact angles do not decrease linearly with increasing hafnium contents. For concentrations below 1.2% Hf, the decrease is slight but continuous with increasing amounts of Hf. Between 1.2% and 1.6% Hf, there is a sudden 18° reduction in θ , and above 1.6% Hf there is no further change (to nearly 2.0% Hf). The decreases in contact angles can be related to the nucleation and growth of HfO_2 grains on the surface of the Al_2O_3 substrates. The primary source for the oxygen is the Al_2O_3 substrate

Figure 6: SEM Views of the Bottom Surface of the Sessile Drop Containing 1.6% Hf. (A) shows a Hf map at Zones 1 and 2; (B) (C) (D) show enlarged secondary electron images of these zones.

which reacts with the Hf in the melt according to the following reaction:

Analysis of the layer proved to be pure HfO_2 , and it is presumed that the Al is released into the melt. For sample compositions below 1.2% Hf, the HfO_2 layer is discontinuous. For samples containing 1.2% to 1.4% Hf, the HfO_2 grains, which are about 0.5 to 2 μ in diameter, are sufficiently numerous to form a nearly continuous layer. At and above 1.6% Hf, the layer appears to be continuous, and thus serves as a diffusion barrier which hinders the formation of additional HfO_2 . These results contrast with those of Zr additions to Ni melted on Al_2O_3 , where a porous ZrO_2 layer was formed, and where the reaction with the Zr in the melt would proceed to completion⁽⁶⁾.

The HfO_2 layer is less than 1 μ in thickness and also serves as a parting agent between the drop and substrate during cooling. The layer appears to be of uniform thickness under Zones 1 and 2 of the drop for compositions at and above 1.2% Hf. The HfO_2 layer adhered mainly to the substrate in the 1.2% Hf sample, whereas in the 1.6% Hf sample, the layer adhered to the drop in Zone 1, and about equally to both the drop and substrate in Zone 2. Thus the adherence of the HfO_2 layer to either the drop or substrate surface depends on

Figure 7: SEM Views of the Al_2O_3 Surface in Contact with the Sessile Drop Containing 1.6% Hf. (A) shows a Hf map of Zones 1, 2, and 3; (B)(C)(D) show enlarged secondary electron images of these zones.

both the melting sequence of the sample and on the Hf content.

Conclusions

- (1) The addition of Hf to MAR M-200 promotes wetting between the alloy and Al_2O_3 substrates (or crucible materials).
- (2) The lowering of the contact angle is not proportional to the Hf content in the alloy, but depends more on the formation of a HfO_2 layer at the interface.
- (3) The greatest decrease in contact angle occurs between 1.2% and 1.6% Hf where the nucleation and growth of HfO_2 grains at the interface form a continuous layer, which in turn hinders the formation of additional HfO_2 .

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