THE EFFECTS OF BERYLLIUM ADDITIONS ON THE OXIDATION OF NICKEL ALUMINIDE AND TITANIUM ALUMINIDE BASED INTERMETALLICS

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ABSTRACT

The effects of Be additions on the oxidation behavior of β-NiAl in moist air at 1000°C and borderline alumina-forming γ (TiAl) + Laves Ti-Al-Cr based alloys at 800°C and 1000°C in dry and moist air were investigated. The addition of Be to β-NiAl suppressed the formation of transient alumina, and resulted in the formation of a protective $BeAl_2O_4$ spinel phase. In dry air, the addition of Be to the Ti-Al-Cr alloys also resulted in the formation of a protective $BeAl_2O_4$ spinel phase. In moist air, only Ti-Al-Cr-Be alloys with a high Cr content (10 to 15 a/o) formed the protective $BeAl_2O_4$ scale.

INTRODUCTION

Beryllium is attractive as an alloying addition to improve the performance of intermetallics because of its low density and the protective nature of its oxide. Unfortunately, due to the health hazards of handling beryllium and its compounds, very little research on the oxidation of Be alloys has been reported to date. We have conducted some selected studies to determine the potential of minor Be additions to improve the mechanical and oxidative properties of intermetallics. In this paper, we will report the results of our survey of the effects of Be on the oxidation resistance of alloys based on the Ni-Al and Ti-Al-Cr systems.

The high temperature oxidation of binary NiAl has been the subject of numerous studies, both because of its use as a coating and its potential application as a structural material. (e.g. references 1-4) The use of NiAl as a monolithic material is severely restricted by its lack of low temperature ductility and poor high temperature creep resistance (5,6). One of the routes for improving properties at all temperatures is alloying with ternary elements which may substitute for Al, i.e. elements which form B2

compounds with Ni (7). Most of these have been thoroughly investigated with the notable exception of Be, which has only been added at very low levels (8,9) . NiBe has been reported to exhibit oxidation kinetics comparable to pure NiAl when exposed in dry oxygen (10). We have determined that there is significant apparent solubility of Be in NiAl. (10). The isothermal oxidation kinetics of alloys containing 0, 1, 3, 5, and 10 % beryllium exposed in dry oxygen have been previously reported (11). In the present work, we have investigated the effects of moisture on the oxidation resistance of these alloys, since water vapor is known to accelerate the oxidation of Be (12) .

Two-phase TiAl (γ) + Ti(Cr,Al)$_2$ (Laves) alloys are under consideration as oxidation-resistant coatings for the γ class of titanium aluminides due to their ability to form a continuous, protective alumina scale (14-16). They also hold promise as a potential oxidation-resistant structural alloy, but are limited by poor room temperature fracture toughness. Reduction in the Al and Cr content may result in improved room temperature toughness, but would certainly be accompanied by loss of the ability to form a protective alumina scale. To restore the ability of a low Al/Cr γ + Laves alloy to form alumina, further alloying additions are needed. Be is a possible choice because it forms a TiBe$_2$ Laves phase, which may behave in a similar manner to the TiCr$_2$ Laves phase with regards to high Al solubility and excellent oxidation resistance (17,18).

EXPERIMENTAL

Ni-Al-Be alloys based on Ni-50Al containing 0, 1 ,2, 5, 7.5, and 10 atomic percent (a/o) Be substituted for Al were selected for study. X- ray diffraction indicated that additions up to 7.5 a/o Be were single-phase NiAl with Be in solution. The Ni-40Al-10Be alloy was primarily β-NiAl with a minor volume fraction of NiBe.

The ternary Ti-Al-Cr alumina-formation boundary defined by Perkins and Meier (14) was used to guide selection of the Ti-Al-Cr-Be alloys (Fig. 1). (Note that the compositions plotted in Fig. 1 are based only on the Al and Cr contents in order to highlight their locations relative to the ternary Ti-Al-Cr alumina formation boundary). The compositions selected for study were Ti-50Al-12.5Be, Ti-45Al-7.5Cr-7.5Be, Ti-45Al-15Cr-Be, and Ti-47.5Al-10Cr-5Be. The Ti-50Al-12.5Be alloy was selected to determine if there was a γ + Ti(Be,Al)$_2$ analogue to the alumina-forming γ + Laves Ti-Al-Cr alloys (17). The remaining three alloys fall at or below the alumina-formation boundary based on the ternary Ti, Al, Cr contents alone (Fig. 1).

The alloys were prepared by arc-melting and casting from high-purity elemental material. After a homogenization anneal at 1200° C for 168 hours, specimens were cut from the ingot and the surfaces were prepared by grinding to a 600 grit finish. The homogenization anneal was effective for the Ni-Al based alloys, but resulted in an extremely coarse (1mm and greater grain size) microstructure in the Ti-Al based alloys.

Samples were placed into a tube furnace and given an isothermal exposure at peak temperatures of 800 and 1000°C for 100 hours in dry air or air saturated with moisture by bubbling through a water column at 20°C. Oxidized samples were characterized by x-ray diffraction (XRD), optical microscopy, and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) mapping. Flat slabs of the oxidized NiAlBe and TiAlCrBe samples were used for phase determinations by x-ray diffraction (XRD). A Scintag XDS2000 diffractometer with a Cu $K\alpha$ source was used at 45kV and 40mA. Continuous scans of two-theta from 20° to 100°, with a step size of 0.02°, were acquired at a rate of 0.6°/minute. Peaks were identified with the aid of JCPDS cards, XRD modeling (CaRIne software), references, and phase diagrams

RESULTS AND DISCUSSION

Ni-Al Based Alloys

The substitution of Be for Al in NiAl was previously shown to suppress the formation of transient (non α) aluminas through the formation of a protective $BeO*Al_2O_3$ ($BeAl_2O_4$) spinel phase during short term (16 h) isothermal exposures from 800-1200°C in dry oxygen (11). In the present study, the oxidation behavior of the Be modified NiAl alloys was investigated for 100 h at 1000°C in moist air. Although water vapor is known to accelerate the oxidation of Be (12), no adverse effects of water vapor on the oxidation of the Ni-Al-Be alloys were observed.

After exposure for 100 h at 1000°C in moist air, the binary NiAl alloy exhibited a characteristic granular surface structure typical of the oxidation of β-NiAl in this temperature range (Fig. 2). This granular surface structure is associated with the formation of transient alumina during the initial transient stages of oxidation(7) . In contrast, the Be modified NiAl alloys exhibited a planar, nearly transparent surface oxide in which the underlying substrate grain structure was clearly visible (Fig. 2). This morphology is similar to that formed in dry oxygen (11). Therefore, the addition of only 1 a/o Be (the lowest level studied) appears to successfully suppress transient alumina formation at 1000°C in both dry oxygen and moist air.

Results from x-ray diffraction of the oxidized alloys are summarized in Table I. Peaks corresponding to β-NiAl were observed on all of the NiAl + Be samples. The NiAl was noticeably textured with preferred orientations in the (110) and (112) planes. Interestingly, upon oxidation, the NiAl (002) peaks were severely reduced to nondetectable intensities.

The binary NiAl sample oxidized to form α-Al_2O_3 after 100 h at 1000°C in moist air. The addition of only 1 a/o Be resulted in the formation of the $BeAl_2O_4$ spinel rather than the α-Al_2O_3. The spinel was found to form on the alloys containing up to 7.5 a/o Be,

but was not detected in the 10 a/o Be sample. In the scale formed on the 10 a/o Be alloy, an unidentified oxide phase (designated X) was observed. The X phase may be $3BeO*Al_2O_3$ based on the pattern published by Galakhov (13), although the match is poor and the major peaks were shifted by as much as 1°. The X phase was also observed on the 5 and 7.5 Be alloys.

Table I: Phases identified by XRD in Ni(Al, Be) alloys after exposure for 100 h at 1000°C in moist air.

Alloy Composition a/o			Phases Identified
Ni	Al	Be	
50	50	0	$NiAl + \alpha\text{-}Al_2O_3$
50	49	1	$NiAl + BeAl_2O_4$
50	48	2	$NiAl + BeAl_2O_4$
50	45	5	$NiAl + BeAl_2O_4 + X$
50	42.5	7.5	$NiAl + BeAl_2O_4 + X$
50	40	10	$NiAl + X$

Ti-Al and Ti-Al-Cr Based Alloys

The oxidation behavior of the Be modified TiAl and Ti-Al-Cr alloys was screened in dry air at 800°C or 1000° C. Only the alloys which exhibited adherent, protective scales in dry air were evaluated in moist air at 1000°C. The results of XRD studies of the oxidized alloys are shown in Table II. In addition to the major phases, there were numerous unidentified peaks which appear to correspond to Ti based oxides. These are listed as "other".

Table II- Phases identified by XRD on Be modified Ti-Al and Ti-Al-Cr based alloys.

Oxidation Conditions	Alloys (a/o)			
	Ti-50Al-12.5Be	Ti-45Al-7.5Cr-7.5Be	Ti-45Al-15Cr-5Be	Ti-47.5Al-10Cr-5Be
Dry Air 800°C	TiAl, other	TiAl, $BeAl_2O_4$	TiAl, Laves, $BeAl_2O_4$	TiAl, Laves, $BeAl_2O_4$
Dry Air, 1000°C	SPALLED TiAl, TiO_2, Al_2O_3, $BeAl_2O_4$	TiAl, $BeAl_2O_4$	TiAl, Laves, $BeAl_2O_4$, other	TiAl, Laves, $BeAl_2O_4$, other
Most Air,	Not Run	SPALLED	TiAl, Laves,	TiAl, Laves,

1000°C			BeAl$_2$O$_4$, other	BeAl$_2$O$_4$, other

The Ti-Al-Cr-Be alloys all had γ-TiAl as the major phase. Alloys with 10-15 a/o Cr also contained significant quantities of the hexagonal C14 Laves phase, Ti(Cr,Al)$_2$. It has yet to be determined whether the Be segregates preferentially to the γ or Laves phases.

The poor oxidation behavior of Ti-50Al-12.5Be suggests that an oxidation-resistant γ + Laves TiAl + Ti(Be,Al)$_2$ analogue to the alumina-forming γ + Laves Ti-Al-Cr alloys may not exist (Fig. 1). However, when added to the borderline alumina-forming Ti-Al-Cr alloys, Be resulted in the formation of the BeAl$_2$O$_4$ spinel phase (Fig. 3), which was shown to be protective when formed on Ni(Al,Be) alloys (11). Therefore, it appears that Be additions to the borderline alumina-forming Ti-Al-Cr alloys show promise for improved oxidation resistance.

A detrimental effect of moisture in air was observed at 1000°C, but only for the Ti-45Al-7.5Cr-7.5Be alloy. Previous work showed that water vapor detrimentally effects the oxidation resistance of Cr modified single-phase γ alloys at 1000°C in air, but not two-phase γ + Laves Ti-Al-Cr alloys (18). The XRD analysis indicated that Ti-45Al-7.5Cr-7.5Be is primarily single-phase γ. Therefore, the poor oxidation resistance of Ti-45Al-7.5Cr-7.5Be in moist air is consistent with this previous work.

Finally, it should be noted that although mechanical property measurements were not made, extensive cracking was observed in the Be containing alloys. Therefore, it would appear that no improvement (in fact, degradation) in mechanical properties was imparted by alloying Ti-Al-Cr alloys with Be at the levels investigated.

SUMMARY

The effects of Be additions on the oxidation behavior of β-NiAl in moist air at 1000°C and borderline alumina-forming γ + Laves Ti-Al-Cr based alloys at 800°C and 1000°C in dry and moist air were investigated. The preliminary results of this study suggest:
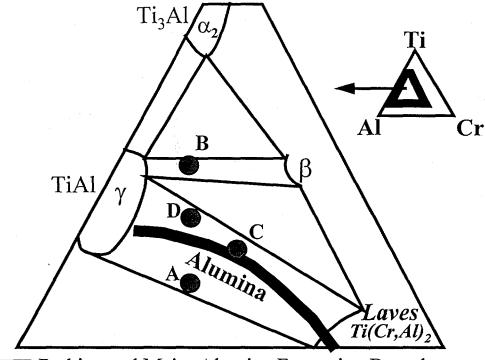
1) Additions of only 1 a/o Be to β-NiAl and borderline alumina-forming γ + Laves Ti-Al-Cr alloys result in the formation of an apparently protective BeAl$_2$O$_4$ spinel phase. This shows that Be is a very mobile element in these alloys.

2) The presence of moisture in air at 1000°C showed no detrimental effect on the oxidation resistance of Be modified β-NiAl alloys.

3) The presence of moisture in air at 1000°C detrimentally affected the oxidation resistance of a primarily single-phase Cr and Be modified γ alloy, but had no detrimental

effect on the oxidation of two-phase γ + Laves Ti-Al-Cr Be alloys.

4) There appears to be no oxidation-resistant TiAl + Ti(Be,Al)$_2$ analogue to the alumina-forming γ + Laves Ti-Al-Cr alloys.

5) The addition of Be to borderline alumina-forming γ + Laves Ti-Al-Cr alloys appears to degrade room temperature mechanical properties (decreased crack resistance).

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■ Perkins and Meier Alumina Formation Boundary

A: Ti-50Al-12.5Be
B: Ti-45Al-7.5Cr-7.5Be
C: Ti-45Al-15Cr-5Be
D: Ti-47.5Al-10Cr-5Be

Figure 1- Schematic 800-1000°C Ti-Al-Cr phase diagram (15) showing alloys selected for study. Note that the Ti-Al-Cr-Be alloys are schematically plotted based on the Al and Cr contents only, and that Ti-50Al-12.5Be is plotted as Ti-50Al-12.5Cr.
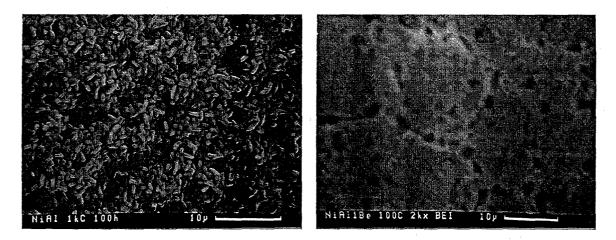
Figure 2: SEM (backscatter mode or secondary mode?) surface micrographs of β-NiAl (left) and Ni-49Al-1Be (right) after exposure for 100 h at 1000°C in air saturated with moisture at 20°C.
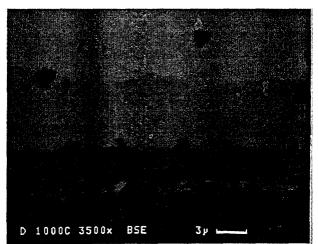

Figure 3: SEM (back-scatter mode) cross section of alloy Ti-47.5Al-10Cr-5Be showing the scale (at bottom) consisting of mostly $BeAl_2O_4$. An Al (and possibly Be) depleted, Cr rich region is visible behind the scale.