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Bonding of the Oxides of High Temperature Alloys

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ABSTRACT

Tensile tests of the bonds formed by sintering together preoxidized metal surfaces indicate that the rate of oxide bonding is determined principally by the rate of metal ion migration through the oxide. For the nickel-base alloys, Inconel X, Inconel 600, Udimet 500, and Udimet 700, for which the oxide is essentially Cr_2O_3, the strengths of the bonds are all of the same magnitude, and secondary alloying additives have only a slight effect. The rate of bonding increases with temperature and decreases as the thickness of the scale formed by preoxidation is increased.

PROBLEM STATUS

With the determination of the rates of bonding of the high-temperature-alloy oxides, further work on the problem has been suspended.

AUTHORIZATION

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BONDING OF THE OXIDES OF HIGH TEMPERATURE ALLOYS

INTRODUCTION

The creep-rupture strength of nickel has been shown to be much higher in air than in vacuum or in an inert atmosphere, and it has been postulated that this enhanced strength is due to the formation and bonding of oxides within incipient cracks. To test this hypothesis, Cass and Achter (1) investigated the strength of the sintered bonds formed between preoxidized nickel specimens. Their results were in complete accord with the hypothesis that sintering of oxides could delay fracture of creep-rupture specimens. A decrease in the rate of sintering was found with longer times of preoxidation and was attributed to the decreased rate of nickel ion migration in the thicker scales.

To determine whether like considerations could explain the high creep-rupture strength of the nickel-base, high-temperature alloys, we made a similar investigation of the oxide bond strengths of Inconel X, Inconel 600, Udimet 500 and Udimet 700. These are all nickel-base alloys with chromium as the principal alloying addition and with varying amounts of cobalt, iron, aluminum, and titanium as secondary additions. All have high but different creep strengths.

EXPERIMENTAL PROCEDURE

As in the previous work, the rupture strength was obtained with hollow metal specimens which were preoxidized, butted together under a load, and then broken in tension. Unlike the previous experiments, however, in the present work the specimens were not cooled to room temperature after preoxidation.

The nominal compositions of the alloys tested are shown in Table 1. Test analyses of the Udimets were well within these nominal limits. The lower halves of the hollow specimens had an outer diameter of 1 in. and an inner diameter of 15/32 in., and were thus thick enough to permit some misalignment error. The upper halves had an outer diameter of 11/16 in. and had a wall thickness of 1/32 in., providing a bearing area of 0.135 in.^{2}.

Table 1
Alloy Composition

Alloy	Composition (wt-%)								
	Ni + Co	Co	Cr	Fe	Ti	Al	Nb	Mn	Mo
Inconel 600	72.0 min	-	14.0-17.0	6.0-10.0	-	-	-	1.0 max	-
Inconel X	70.0 min	1.0 max	14.0-17.0	5.0-9.0	2.25-2.75	0.40-1.00	0.10-1.20	1.0 max	-
Udimet 500	balance	13.0-20.0	15.0-20.0	4.0 max	2.5-3.25	2.5-3.25	-	-	3.0-5.0
Udimet 700	balance	18.0	15.0	0.15	3.5	4.5	-	-	5.0

After grinding the bearing surfaces through 600-grit papers (a finer finish had no apparent effect on ultimate bond strength), the specimens were attached to the threaded

Nimonic grip-rods with rounded nuts and washers which permitted some rocking motion of the specimen halves during both sintering and tensile testing. Specimens and grip-rods are shown in Fig. 1. The grip-rods with the attached specimens were then inserted into the grips of an Instron tensile testing machine. The grip-rods were held in alignment by guides attached to the Instron frame, the frame also holding a preheated Hevi-Duty split furnace vertically at the proper position. The specimens usually attained the test temperature within five minutes. Temperatures were measured with a chromel-alumel thermocouple inserted in a 1/16-in. hole drilled in the lower specimen half, and controlled to within ±1/4°C by a chromel-alumel thermocouple on the furnace windings.

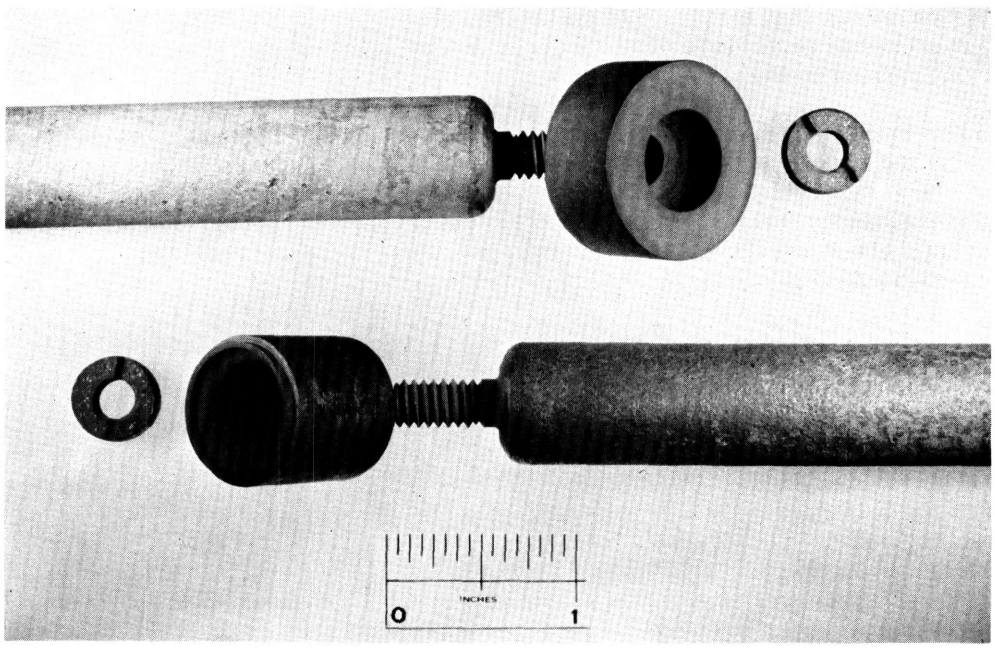

Fig. 1 - Oxide bond specimens and grip-rods. The specimens are attached to the threaded rods by the rounded nuts.

After preoxidation in ambient air for the required time, the specimen halves were run together and bonded under a constant load which was maintained to within ±1 lb by the load-cycling cams of the Instron machine. If tensile testing was conducted at the same temperature as preoxidation and sintering, the cross-head of the tensile machine was immediately lowered at a predetermined speed until fracture; if testing was conducted at temperatures other than that of preoxidation and sintering, this temperature was attained with the specimens maintained under load. Complete spalling of the oxide scales invariably occurred in all specimens cooled to room temperature and precluded any metallographic examination of the sintered bond. It is believed, however, that the structure was similar to that of the pure nickel specimen shown in Fig. 2. It will be noted that the bonded interface is clearly delineated by a string of flattened pores.

RESULTS

Although stress-strain plots were obtained for each specimen, it soon became apparent that the fracture of the oxide bond was almost completely brittle and that the observed elongations occurred principally in the grips. Thus, the only significant data that

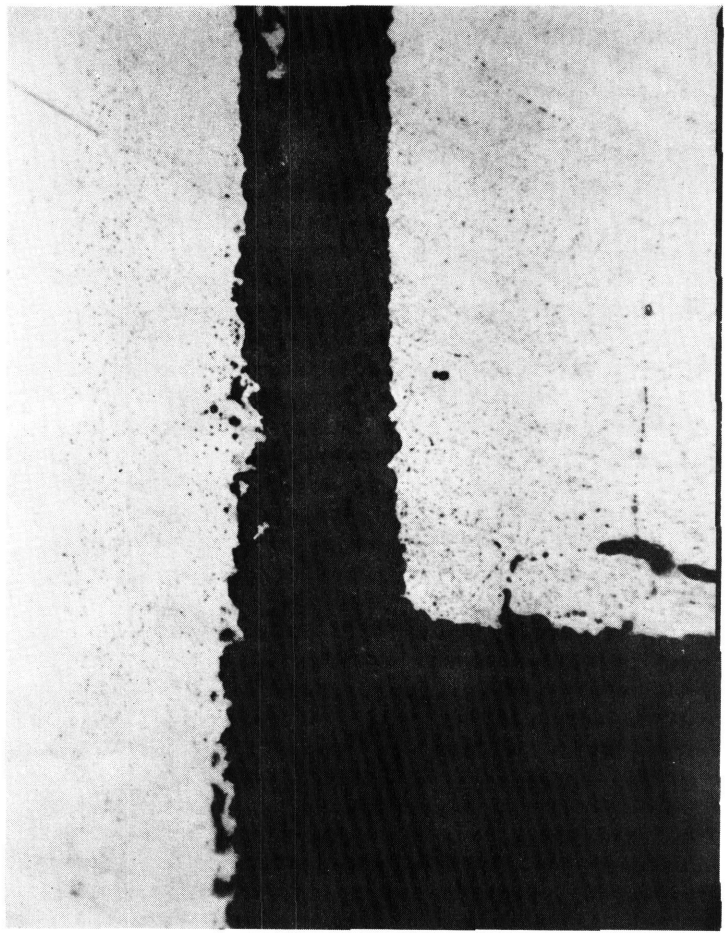

Fig. 2 - The interface of a nickel oxide-bond specimen after 19 hours of preoxidation and 24 hours of sintering under a 370-psi load at 900°C

could be measured were the ultimate fracture stresses. Fracture invariably occurred at the oxide-oxide interface even at the longest times and highest temperatures of sintering. The sintered interface obviously remained a plane of weakness even after the bond attained its limiting strength, although oxidation of the fractured surfaces (almost invariably spalled) occurred so rapidly that no clue could be obtained to the extent of sintering by metallographic examination.

To test the validity of the present experimental procedures, which varied in some respects from the earlier work, a limited number of tests with pure nickel were carried out. Some of the data are presented in Table 2. The present results vary to some degree from the earlier ones. At 817°C, the testing temperature of the previous work, sintering was obviously erratic and consistent results could be obtained only by sintering and testing at 900°C. Likewise, the fracture stresses at similar times of sintering were somewhat lower than the earlier results even though obtained at a higher temperature.

Preliminary experiments with the four alloys established that sintering at any temperature below 900°C was incomplete and yielded only erratic results, and that results obtained by sintering at a higher temperature, followed by cooling to below 900°C, were also erratic, probably due to spalling of the oxides. Since testing above 1000°C was

Table 2
Comparison of the Fracture Stresses of Oxide-Bonded Nickel as Obtained by Cass and Achter (1) and of the Present Work

	Cass and Achter	Present Work	Cass and Achter	Present Work
Test temperature	817°C	900°C	817°C	900°C
Preoxidation time	5 hr	7 hr	5 hr	7 hr
Sintering time	16 hr	16 hr	90 hr	88 hr
Sintering load	100 psi	74 psi	100 psi	74 psi
Fracture stress	2300 psi	1320 psi	2600 psi	2300 psi

impracticable due to stretching of the Nimonic grip-rods, systematic testing was therefore confined to the temperature range 900-1000°C. Although considerable alloy depletion occurred in the metal at the oxide interface, it was found possible to reuse the specimens by deep grinding and to duplicate results obtained with pristine specimens. In most cases, but not all, the data represent an average of 2 to 4 tests. The range of results was usually within 10 to 25 percent of the average, and a greater deviation could usually be traced to badly aligned specimens. For instance, in Table 3, the 1200-psi value for Udimet 500 at 16 hours is the average of 1150, 1580, and 925 psi.

For convenience, comparison of the bond strengths of the four alloys was carried out under a standardized test procedure consisting of a 7-hour preoxidation and a 16 to 64 hour bonding treatment and with fracture testing at a cross-head speed of 0.002 in./min. The data obtained under these conditions are presented in Tables 3 and 4.

Table 3
Data Obtained with Specimens Preoxidized for 7 Hours, Sintered Under a 370-psi Load and Fractured at 900°C

Material	Sintering Time (hr)	Fracture Stress (psi)
Udimet 700	16	1140
Udimet 500	16	1200
	64	1640
Inconel X	16	1330
	64	1460
Inconel 600	16	1050
	64	1520

Although not as extensive as that in the above tables, sufficient data, presented in Table 5, was gathered to indicate a profound effect of the time of preoxidation. For comparison, pertinent data drawn from Table 3 are included.

Table 4
Data Obtained with Specimens Preoxidized for 7 Hours and Sintered Under a 370 psi Load at 1000°C. The Tensile Tests Were Carried Out at 900°C.

Material	Sintering Time (hr)	Fracture Stress (psi)
Udimet 700	16	1330
	64	1500
Udimet 500	16	1400
	64	1560
Inconel X	16	1400
	64	1780
Inconel 600	16	1120
	64	1600

Table 5
The Effect of Preoxidation Time on Fracture Stress at 900°C

Material	Preoxidation Time (hr)	Sintering Time (hr)	Fracture Stress (psi)
Ni	2	16	1400
	7	16	1320
Udimet 500	7	16	1200
	54	16	740
Inconel 600	7 (1000°C)	16 (1000°C)	1320
	19	24	890

The majority of these data were obtained with a cross-head speed of 0.002 in./min. However, a number of runs were made at stress-rates varying from 0.02 in./min to 0.0002 in./min with no detectable change in the fracture stress, indicating an almost completely brittle fracture. Likewise, no effect of variation in the sintering load from 74 psi to 700 psi was noticed, which might indicate that plastic flow plays no part in oxide bonding.

The following conclusions are drawn from the above tables:

1. Alloying with secondary additives appears to have only a negligible effect on the rate of bonding.

2. The strength of the bonds decreases markedly as the time of preoxidation is increased.

3. The rate of bonding increases with sintering temperature, even though the thickness of the scale must also increase at the same time.

4. No effect of the rate of stress application on fracture stress is apparent.

5. Within limits, the rate of bonding is independent of the applied load.

DISCUSSION AND CONCLUSIONS

The oxidation processes of even simple Ni-Cr alloys such as Inconel 600 have not yet been completely elucidated, but it has been determined (2) that the scales are composed of Cr_2O_3 overlying a layer of mixed Cr_2O_3 and an NiO-Cr_2O_3 spinel. Alloying with Ti and Al in the high-temperature alloys (in addition to strengthening the metal by forming precipitates of $(Al,Ti)Ni_3$, carbides, and nitrides and by internal oxidation) adds greatly to the complexity of the oxidation process. But it appears that, as in the simple alloys, the scales are composed of Cr_2O_3 and of complex spinels, but not necessarily appearing in any simple sequence. According to Wlodek (3), a thin film of α Al_2O_3 is first formed, followed by the appearance of Cr_2O_3 and of complex spinels with all the alloying additions appearing distributed throughout the scale. It is not clear whether the spinels and the as-yet unidentified oxides extend to the oxide surface. It is possible that partial spalling followed by direct permeation of oxygen to the metal-oxide interface occurs continuously. Decompositions of the oxide at the spinel interface accompanied by diffusion of oxygen through pores has also been suggested (4).

In the present work, just as in pure nickel, the decreased rate of bonding of thicker scales suggests that the migration of metal ions through the scale is the principal determinant of the rate of bonding. The secondary additions, Nb, Al, and Ti, to the basic Fe, Ni, Cr alloy, Inconel 600, have but little effect on the rate of bonding. This is borne out by the results of Hagel (5) who could find no difference between the diffusivity of Cr in pure Cr_2O_3 and that in Cr_2O_3 alloyed with CrO_2 and Y_2O_3. Although Wenderott (6) reports an increased rate of diffusion of Cr in Cr_2O_3 containing the same additions, his conclusions are based on the sintering of Cr_2O_3 powders. A consideration of the present experiments suggests that bonding of oxidized metal is a process quite different from ordinary powder sintering, where rates are determined by curvature, and more nearly like that taking place in a diffusion couple in which rates are a function of concentration gradient. In the present experiments, the concentration gradient would be established by the equilibrium concentrations at the metal-oxide and the oxide-gas interfaces and would decrease as the oxide layers increased in thickness. Further, spalling, which would occur more often in the thicker scales, would also tend to decrease the gradient, since direct penetration of oxygen through the pores would saturate the inner layers and reduce the concentration gradient to zero at the bonding interface. Although it is possible that complex spinels are present in conjunction with Cr_2O_3 at the bonding interface, in spinels, as in Cr_2O_3, the metal ions are the most mobile species (7); thus the rate of bonding of spinels would be determined by the same factors as the bonding of Cr_2O_3.

Although the scales are of a completely different nature, it is possible that, as in nickel, oxide bonding can play a role in determining the creep and fatigue strength of the high-temperature alloys, a process whose rate is determined by the rate of migration of metal ions through the scale. However, the lack of any clear-cut effect of alloying suggests that the secondary alloy additions have their principal influence on the internal precipitates and not on the bonding mechanism.

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(PAGE 2)

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