THERMOGRAVIMETRIC STUDY OF THE REDUCTION OF OXIDES PRESENT IN OXIDIZED NICKEL-BASE ALLOY POWDERS[*]

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ABSTRACT

Carbon, hydrogen, and hydrogen plus carbon reduction of three oxidized nickel-base alloy powders (a solid solution strengthened alloy both with and without the γ' formers aluminum and titanium and the solid solution strengthened alloy NiCrAlY) were evaluated by thermogravimetry. Hydrogen and hydrogen plus carbon were completely effective in reducing an alloy containing chromium, columbium, tantalum, molybdenum, and tungsten. However, with aluminum and titanium present, the reduction was limited to a weight loss of about 81%. Carbon alone was not effective in reducing any of the alloys, and none of the reducing conditions were effective for use with NiCrAlY.

SUMMARY

This study was carried out to determine the effect of controlled carbon, hydrogen, and hydrogen plus carbon reduction of the oxides present in oxidized nickel-base alloy powders. The successful reduction of these oxides, which are present to a greater or lesser extent in all powder metallurgy processed nickel-base materials, would be beneficial for all superalloys prepared by powder techniques. These techniques could be particularly important in developing oxide-dispersion-strengthened alloys prepared by either wet or dry grinding. The materials studied were powder samples of a solid-solution-strengthened nickel-base alloy containing chromium, columbium, tantalum, molybdenum, and tungsten both with and without the γ'-forming elements aluminum and titanium and powder samples of the solid-solution-strengthened alloy NiCrAlY. The powders were deliberately oxidized for 6 h at 1100°C in pure oxygen. Reductions were carried out in a thermogravimetric analysis (TGA) apparatus. Sample heating was linear with time and at a constant rate of 3 Celsius degrees per minute from ambient to 1200°C. The reducing agents were carbon, dry hydrogen, and a combination of the two. The extent of reduction was

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evaluated by weight-loss data and by X-ray analysis of the reduction residue. All reductions were carried out in duplicate to verify the reproducibility of the reduction curves.

Hydrogen and hydrogen plus carbon were both completely effective in reducing the oxides in the solid-solution-strengthened alloy without the γ'-forming aluminum and titanium. However, these two reductants were not able to completely reduce (weight loss, 78–81 %) the oxides present in the alloy powders containing aluminum and titanium. Carbon alone was not an effective reductant for any of the alloys studied. And none of the reducing conditions were adequate for the highly oxidation resistant alloy NiCrAlY. For alloys of this type, alternative, more effective cleaning procedures must be developed to reduce the $\alpha\text{-}Al_2O_3$ which forms during oxidation.

INTRODUCTION

One of the most serious deterrents to the development of good mechanical properties in dispersion-strengthened superalloys prepared by the wet grinding of metal together with stable oxide powders is the deleterious effect of oxide contamination. Wet grinding frequently produces substantial quantities of unwanted matrix oxides. The author has frequently observed oxygen levels of 10–20 wt. % in wet-ground powders. These oxides ruin the effectiveness of the dispersion by causing the intentionally added fine stable oxide powders to agglomerate[1–3]. As a consequence of this agglomeration, ductility, stress-rupture life, and thermal fatigue properties are reduced[2]. An alternative processing approach, mechanical alloying by dry grinding, has minimized, but not eliminated, this problem by lowering the oxygen pickup to approximately 1–1.5%. Dispersion-strengthened materials produced by this latter process have demonstrated good mechanical properties[4–6]. The dry mixing of coarse (1–10 μm) particles of reactive metals such as chromium, aluminum, and titanium with finely wet-ground nickel plus dispersoid powders has also shown considerable promise for producing dispersion-strengthened alloys with good properties[7]. The potential for using the complete wet grinding approach in which all elements including reactive metals and master alloys are ground together is, however, still considered to be great. This approach has yielded unalloyed nickel plus thoria materials with a fine dispersion[3]. If a method can be found to reduce the bulk of the undesirable oxide contamination in nickel alloys, it should be possible to produce dispersion-strengthened materials with superior strength characteristics by the wet-grinding approach.

The objective of this study was to determine if oxides typical of those formed during the wet grinding of nickel-base superalloy powders could be reduced with carbon, hydrogen, or a combination of the two. The successful reduction of these oxides could lead to the application of the wet-grinding approach to these types of materials; in addition, it could also be of considerable benefit in producing prealloyed powder metallurgy superalloys and mechanically alloyed materials.

The reducing conditions studied in the present investigation were the same as those used in a previous study[8] where it was shown that deliberately oxidized nickel

—20 chromium powder could be effectively reduced with dry hydrogen and dry hydrogen plus carbon. The materials studied in the present investigation were powders of a solid-solution-strengthened nickel-base alloy both with and without the addition of the γ'-forming elements aluminum and titanium and powders of the solid-solution-strengthened alloy NiCrAlY. The powders were deliberately oxidized for 6 h at 1100°C in pure oxygen to produce a controlled starting condition. The reducing conditions were carbon, dry hydrogen, and a combination of the two. All reductions were carried out under controlled conditions in a thermogravimetric analysis (TGA) apparatus which has been described previously[8, 9]. Reductions were evaluated by weight-loss data and by X-ray evaluation of the reduction residue from each experiment. All reductions were carried out in duplicate to verify the reproducibility of the reduction curves.

MATERIALS, APPARATUS, AND PROCEDURE

Materials

The materials used in this study were inert-gas-atomized nickel-base alloy powders, spectrographic grade lampblack, ultra-high-purity hydrogen, research grade helium, and research grade oxygen. The chemical analyses of the three nickel-base alloy powders are shown in Table 1. Alloy 1 was analogous to conventional solid-solution-strengthened nickel-base alloys; alloy 2 was essentially the same as alloy 1 but contained the γ'-forming elements aluminum and titanium; alloy 3 was the highly oxidation resistant solid-solution-strengthened alloy NiCrAlY. All the metal powders used in this study were in the size range of —200 to +325 mesh (74–44 μm). The lampblack was —325 mesh.

Table 1
CHARACTERISTICS OF STARTING ALLOY POWDERS

Alloy no.	Composition (wt. %)									
	Al	Cr	Ni	Co	Ta	Mo	W	Ti	Y	O₂
1 (Solid solution)		18.59	Balance	1.24	1.25	3.92	4.30			0.11
2 (Solid solution plus γ')	4.15	14.86	Balance	1.18	1.30	3.95	4.33	3.41		0.05
3 (Solid solution)	5.30	16.21	Balance						0.17	0.01

For the purpose of the reductions carried out in this study, all three alloy powders were given an identical preoxidation treatment which consisted of heating in an aluminum oxide crucible for 6 h at 1100°C in pure, research grade oxygen. Oxidized rather than wet-ground powders were used for the following reasons.

(1) At the time the work was carried out, it was not possible to determine accurately the oxygen content of powders containing large amounts (greater than 10%) of oxygen; however, the oxygen content could be determined accurately by measuring weight-gain during oxidation.

Table 2

OXYGEN CONTENT OF ALLOY POWDERS
OXIDIZED AT 1100°C FOR 6 h. IN OXYGEN

Alloy no.	Oxygen content (wt. %)
1	11.4
2	15.1
3	3.2

(2) Powders ground in hydrocarbon grinding fluids invariably contain a considerable amount of carbon contamination which would have made it impossible to evaluate the effect of hydrogen as a reducing agent.

(3) Grinding in water, which would have eliminated the problem of carbon contamination, was not considered to be practical for the alloys studied.

The oxygen content based on weight gain plus the initial oxygen content of the powders is shown in Table 2. Note that alloy 3 formed much less oxide than either alloy 1 or alloy 2.

The oxidized alloy powder plus carbon mixtures necessary for the carbon reduction experiments were prepared by dispersing weighed amounts of the constituents in 200 proof alcohol followed by air drying at 100°C. Upon completion of the drying step, the powders were stored in a desiccator until used. About 20 g of each blend were prepared. The amount of carbon added was just sufficient for the stoichiometric conversion of the oxygen to carbon dioxide (CO_2). Selection of this carbon addition was based on the results of a study[8] which showed that this stoichiometric carbon addition yields the most complete reduction.

Apparatus

The essential features of the TGA apparatus used in this study are described in refs. 8 and 9. A schematic drawing of the balance and reaction tube assembly, which are the primary components of the TGA system, is shown in Fig. 1.

Procedure

The sample to be reduced was weighed directly into the crucible on an auxiliary balance located outside the TGA system. Weighing was done to the nearest 0.1 mg. The amount of material in the samples was determined from the oxygen content of the powder to give a weight loss of close to 10 mg upon complete removal of the oxygen and, where present, the added carbon.

The crucible containing the sample was attached to the quartz support fiber which was suspended from the balance. After closing and evacuating the system, it was backfilled with the desired atmosphere, i.e. hydrogen for the hydrogen and hydrogen plus carbon reductions, and helium for the carbon reduction. The flow rate of the reaction gas was, in all cases, 150 ml/min. The reaction gas (hydrogen) and the purge gas (helium) were purified by the procedures described in ref. 9.

Before conducting the experimental reduction runs, a buoyancy calibration run was carried out to correct for changes in density of the flowing gases and other
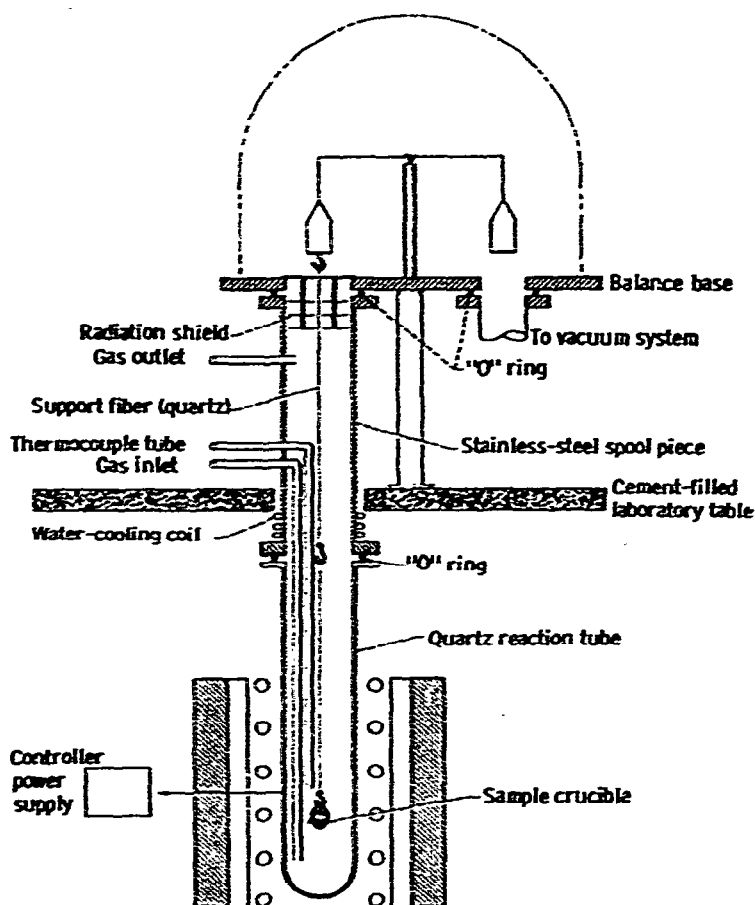
Fig. 1. Balance and reaction tube assembly.

fluctuations that occur as a function of temperature. In all cases, the purge gas flow rate was 50 ml/min helium. The heating rate was linear in all cases and at a constant rate of 3 Celcius degrees per minute from ambient to 1200°C. A separate temperature against time curve was obtained for each experimental run to verify the linearity of the temperature program. At least two experimental reduction runs were made for each alloy/reducing agent combination to verify the reproducability of the reductions.

RESULTS AND DISCUSSION

Table 3 presents a summary of the sample materials, the reducing conditions, and the percent of the calculated weight loss based on the complete reduction of the sample to metal for each run, i.e. complete loss of oxygen and, where present, the deliberately added carbon. The X-ray analysis results and the color of the reduction residue for each run are included in this table.

Weight-loss data presented in Table 3 were obtained from the curves for weight loss as a function of temperature. These curves also represent percent weight loss

Table 3

WEIGHT LOSS[a] AND DESCRIPTION OF RESIDUE[b] FOR CONTROLLED CARBON, HYDROGEN, AND HYDROGEN PLUS CARBON REDUCTION OF OXIDES PRESENT IN OXIDIZED NICKEL-BASE SUPERALLOY POWDERS

		Reducing agent											
		None (as-oxidized)			Carbon			Hydrogen			Hydrogen plus carbon		
			Residue description			Residue description			Residue description			Residue description	
Alloy no.	Alloying elements	Alloy weight loss (%)	Minor phases present	Coloration	Alloy weight loss (%)	Minor phases present	Coloration	Alloy weight loss (%)	Minor phases present	Coloration	Alloy weight loss (%)	Minor phases present	Coloration
1	Cr, Cb, Ta, Mo, W		NiO, Cr_2O_3, $NiCr_2O_4$, M_2O_6		14.3	Cr_2O_3, M_2O_6	Greenish black	103.0	None	Silver metallic	98.3	None	Silver metallic
2	Cr, Cb, Ta, Mo, W, Ti, Al		NiO, Cr_2O_3, $NiCr_2O_4$, M_2O_6		49.4	Cr_2O_3, M_2O_6	Black	80.8	$\alpha\text{-}Al_2O_3$	Black	78.4	$\alpha\text{-}Al_2O_3$	Dark grey
3	Cr, Al, Y		NiO, $\alpha\text{-}Al_2O_3$		10.8	$\alpha\text{-}Al_2O_3$	Black	22.0	$\alpha\text{-}Al_2O_3$	Grey metallic	44.1	$\alpha\text{-}Al_2O_3$	Dull grey

[a] Based on total reduction of sample to metal including removal of added carbon when present.
[b] X-ray analysis of minor phases present (all samples indicated a nickel solid solution was major phase present) and residue coloration.
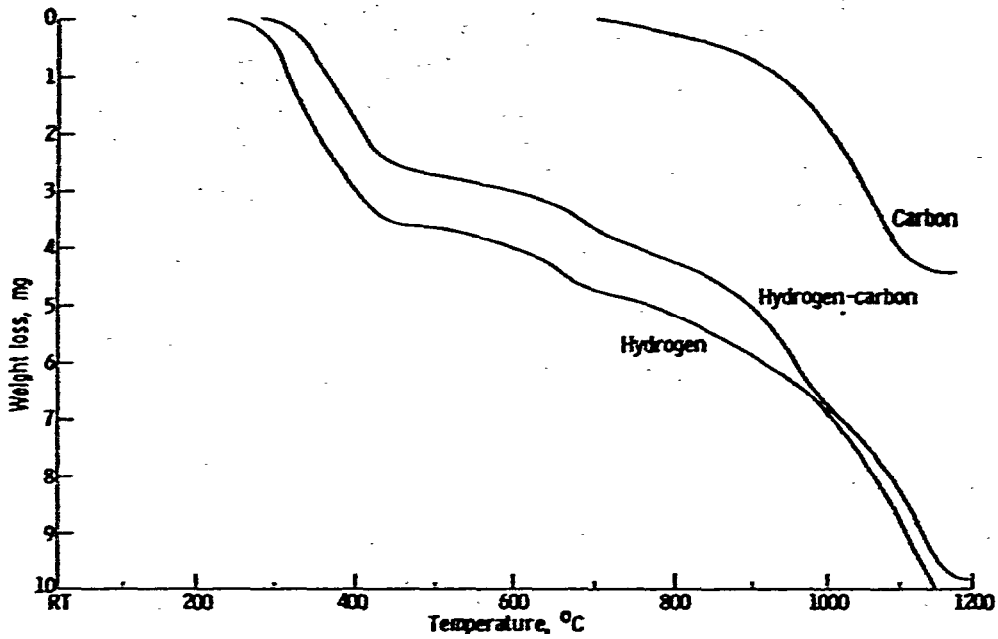
Fig. 2. Controlled reaction of hydrogen, carbon, and hydrogen plus carbon with oxidized alloy 1 containing chromium, nickel, columbium, tantalum, molybdenum, and tungsten.
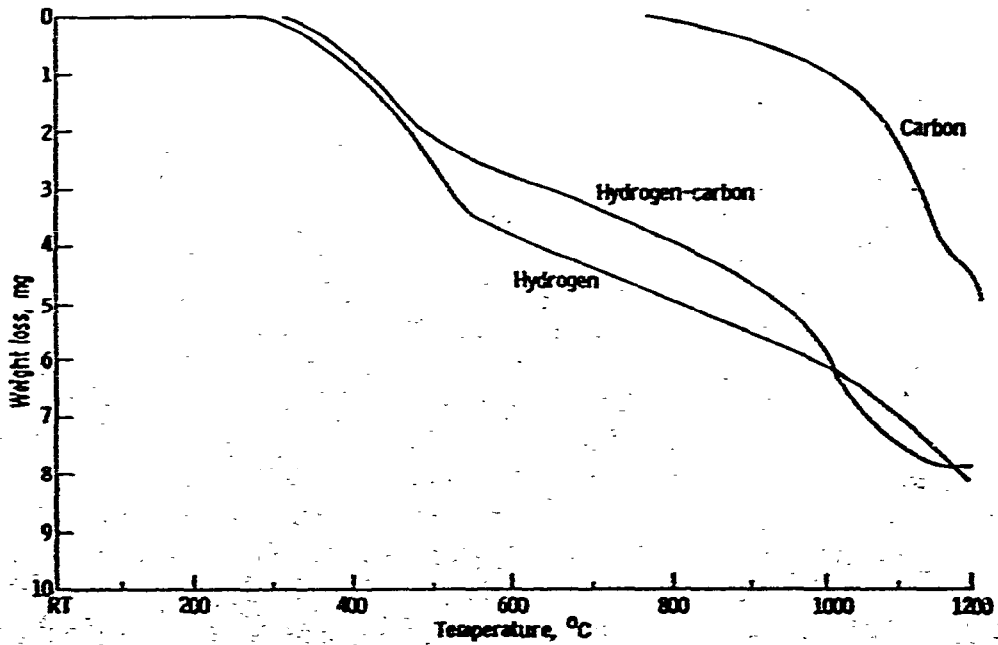

Fig. 3. Controlled reaction of hydrogen, carbon, and hydrogen plus carbon with oxidized alloy 2 containing aluminum, chromium, nickel, columbium, tantalum, molybdenum, tungsten, and titanium.
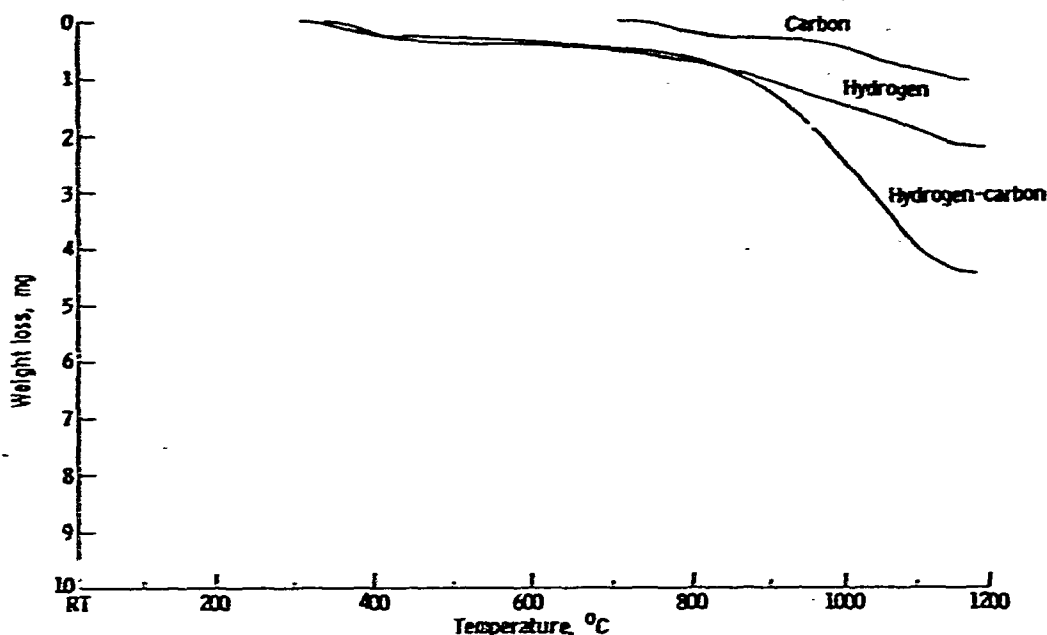
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Fig. 4. Controlled reaction of hydrogen, carbon and hydrogen plus carbon with oxidized alloy 3 containing aluminium, chromium, nickel, and yttrium.

because they have been normalized so that a 10-mg weight loss is equivalent to a weight loss of 100%. The TGA weight loss curves for the carbon, hydrogen, and hydrogen plus carbon reductions of the three nickel-base alloys are shown in Figs. 2–4. Each of the curves presented in these figures has been corrected for the effect of buoyancy.

Reduction of oxidized solid solution alloy (alloy 1)

The chemistry of the solid solution alloy (alloy 1) is shown in Table 1. In the as-oxidized condition, this alloy contained 11.4% oxygen (see Table 2). As shown in Table 3, an X-ray analysis of the oxidized powder indicated the presence of NiO, Cr_2O_3, $NiCr_2O_4$, and M_2O_6 in addition to a nickel solid solution. The M_2O_6 is a tri-rutile structure, sometimes called tapiolite, with M being tantalum or columbium. Carbon reduction of this material was not complete. The maximum weight loss was only 44.3% at 1200°C. The residue was greenish black and the X-ray analysis indicated the presence of Cr_2O_3 and M_2O_6. With hydrogen, the reduction of this material was complete, the weight loss being 103.0% at 1100°C. The reduction value of 103.0% appears to be within the limit of accuracy of the system which, as shown in ref. 8, is of the order of ±2.5% at 1200°C. The residue from this reduction was silver metallic in color and the X-ray analysis indicated only the presence of a nickel solid solution. With hydrogen plus carbon, the reduction was also complete. The weight loss in this case was 98.3% at 1200°C. As with the hydrogen reduction, the color of the residue was silver metallic and the X-ray analysis indicated only the presence of a nickel solid solution.

The weight loss curves shown in Fig. 2 indicate that reduction with carbon did not begin until temperatures in excess of 700°C. The carbon reduction was generally slow with a slightly increased rate occurring between 900 and 1100°C. Beyond 1100°C, the curve was flat, which indicated that the reaction had terminated. This is in marked contrast to oxidized nickel–20 chromium reduced with carbon[8] which probably would have been completely reduced either at temperatures slightly greater than 1200°C or, if held for a sufficient time, at 1200°C. The reason for the weight plateau beginning at 1100°C is not certain. Perhaps it is related to the formation of stable carbides of columbium, tantalum, molybdenum, or tungsten. An X-ray analysis did not reveal the presence of carides. This is perhaps due to the fact that, since only such small amounts were formed, they were below the limit of detection by the X-ray techniques used.

As shown by the weight loss curves, the reduction with hydrogen or hydrogen plus carbon was quite similar. In both cases, the weight loss was initiated at about 250°C and continued to about 1150°C. The most obvious difference between the two reducing conditions was that the weight loss curve for the hydrogen reduction was displaced slightly to the left (lower temperature) of the hydrogen plus carbon curve. This is probably due to the fact that carbon alone does not appear to affect the reduction until temperatures of the order of 700°C are reached. Thus, up to this point, the carbon merely acts as an inert filler material which tends to slow down the reaction. A similar behavior was observed with oxidized nickel–20 chromium as reported in ref. 8. Above 1000°C, the hydrogen and hydrogen plus carbon curves are closer together since this is the temperature range in which the carbon reacts more rapidly. The net result is that carbon is relatively ineffective by itself and tends to hamper the reduction by hydrogen. It may also be noted that the hydrogen plus carbon curve levels off at about 1150°C. And, although no carbides were detected in the residue, the plateau could be associated with the formation of stable carbides.

Despite these observations relative to the effect of carbon, it has been the author's experience that almost all wet grinding of powders is carried out with hydrocarbon solvents. Such a grinding procedure invariably results in the pickup of substantial quantities of carbon. Therefore, the combination of hydrogen plus carbon probably more nearly approximates the conditions which would be expected to prevail in any practical attempt at reduction of wet ground powders.

Reduction of oxidized solid solution plus γ' alloy (alloy 2)

The oxidized solid solution plus γ' alloy (alloy 2) contained 19.1% oxygen. As shown in Table 3, an X-ray analysis of this material indicated the presence of NiO, Cr_2O_3, $NiCr_2O_4$, and M_2O_6 in addition to a nickel solid solution. Reduction of this material was not complete under any of the reducing conditions studied.

Table 3 indicates that the carbon reduction resulted in a weight loss of 49.4%. The residue was black and contained Cr_2O_3, M_2O_6, and a nickel solid solution. As with the solid solution alloy (alloy 1), hydrogen and hydrogen plus carbon appeared to be the most effective reducing agents. The weight losses were 80.8 and 78.4%,

respectively. The residue from the hydrogen reduction was black, and an X-ray analysis indicated the presence of α-Al_2O_3 and a nickel solid solution. With hydrogen plus carbon, the residue was dark grey and contained α-Al_2O_3 and a nickel solid solution.

The failure to observe α-Al_2O_3 in alloy 2 in the as-oxidized condition, despite the fact that thermodynamically it would be expected to form, was probably because its presence was masked by the large amounts of NiO and Cr_2O_3 that were formed during oxidation. In addition, the reflections from α-Al_2O_3 tend to be adsorbed by other compounds such as Cr_2O_3. This would also offer a reasonable explanation for the failure to observe any indication of α-Al_2O_3 in the sample reduced with carbon alone.

Weight loss curves for the reduction of alloy 2 are shown in Fig. 3. With carbon alone, the weight loss was initiated at about 800 °C and continued rapidly up to the maximum temperature of 1200 °C. Although the weight loss was only about 50%, the shape of the curve indicates that longer times and/or higher temperatures would probably have resulted in a greater amount of reduction. The weight loss curves for the hydrogen and hydrogen plus carbon reductions were generally quite similar to those for the same reducing agents as applied to oxidized alloy 1 as shown in Fig. 2, and the same general comments seem to apply. The reason for the increased rate of reaction for the hydrogen plus carbon reduction in the temperature range of 1000–1150 °C is not known.

The significance of the results of the reduction attempts with oxidized alloy 2 is the observation that α-Al_2O_3 once formed during oxidation cannot be reduced by carbon, hydrogen, or the combination of the two. Within the limits of detection by X-ray analysis, the other oxides formed appear to be partially reduced by carbon and completely reduced by hydrogen and hydrogen plus carbon. As with oxidized alloy 1, the benefits to be derived from the use of carbon as the sole reducing agent appeared to be minimal at best.

Reduction of oxidized NiCrAlY (alloy 3)

The third alloy studied, NiCrAlY, was a highly oxidation resistant solid-solution-strengthened alloy. The oxidation resistance of this alloy was demonstrated by the fact that heating for 6 h at 1100 °C in pure oxygen produced an oxygen pickup of only 3.2%. An X-ray analysis of the oxidized material indicated the presence of NiO, α-Al_2O_3, and a nickel solid solution. Failure to detect Y_2O_3 was probably due to the small yttrium content (0.17% as shown in Table 1) of the alloy.

Reduction of oxidized alloy 3 was far from complete under any of the reucing conditions employed in this study. The percentage reductions, as shown in Table 3, were 10.8, 22.0, and 44.1%, respectively, for reduction with carbon, hydrogen, and hydrogen plus carbon. The X-ray analysis of all three reduction residues indicated the presence only of α-Al_2O_3 and a nickel solid solution. The residue from the carbon reduction was black while the residues from the hydrogen and hydrogen plus carbon were dull grey and metallic grey, respectively.

The weight loss curves for the oxidized alloy 3 are shown in Fig. 4. The stability of this material under reducing conditions, particularly carbon or hydrogen alone, is quite evident. With the combination of carbon and hydrogen, however, a greater reduction was observed. As can be seen, with carbon alone the weight loss did not begin until temperatures of the order of 700°C were reached. From about 700°C to the upper temperature limit of 1200°C, the weight loss was slow and continual. Based on the shape of this weight loss curve it does not appear likely that higher temperatures or longer times would have had any pronounced effect on the reduction. With both hydrogen and hydrogen plus carbon, the weight loss began at about 350°C and continued to about 1150°C where a weight plateau was reached. Up to about 850°C, the two curves were essentially the same; however, beyond 850°C, the hydrogen plus carbon reduction resulted in a considerably more rapid weight loss. The shape of these weight loss curves also suggests that longer time and/or higher temperatures would probably not have improved the reduction. As with alloy 2, it seems that α-Al$_2$O$_3$ once formed during the oxidation step cannot be reduced by carbon, hydrogen, or a combination of the two.

SUMMARY OF RESULTS

This study, carried out to determine the effect of controlled carbon, hydrogen, and hydrogen plus carbon reduction of the oxides present in oxidized solid solution and solid solution plus γ'-strengthened nickel-base alloy powders produced the following major results.

(1) Hydrogen and hydrogen plus carbon were completely effective in reducing the oxides present in an oxidized solid-solution-strengthened nickel-base alloy powder containing chromium, columbium, tantalum, molybdenum, and tungsten.

(2) With the addition of aluminum and titanium to the solid-solution-strengthened alloy, the reduction with hydrogen and hydrogen plus carbon was limited to a weight loss of 78–81%. Presumably this was due to the inability to reduce α-Al$_2$O$_3$ formed during oxidation.

(3) Hydrogen and hydrogen plus carbon at temperatures up to 1200°C were not adequate for the removal of oxygen from the highly oxidation resistant solid-solution-strengthened alloy NiCrAlY, which also forms α-Al$_2$O$_3$ on oxidation.

(4) Carbon alone at temperatures up to 1200°C was not an effective reductant for any of the three alloys studied. And in fact it appears that carbon may hinder the hydrogen reduction of those materials that can be reduced with hydrogen alone.

CONCLUDING REMARKS

The results of this study indicate that hydrogen and hydrogen plus carbon can be used to completely clean certain complex solid-solution-strengthened nickel-base superalloys. The same reducing agents are only partially effective for cleaning alloys containing the highly reactive γ'-forming elements aluminum and titanium. Pre-

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sumably, the major problem is that once α-Al_2O_3 is formed by oxidation, carbon hydrogen, or hydrogen plus carbon are not capable of reducing it. Therefore, alternate cleaning procedures must be developed. These might involve the use of halide atmospheres or perhaps hydrides of calcium or yttrium.

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