HORIZONS INCORPORATED
2905 EAST 79TH STREET • CLEVELAND 4, OHIO

Interim Report No. 2

Reinforcement of Nickel Chromium Alloys with Sapphire Whiskers

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Cleveland 4, Ohio

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Written by: Robert H. Kelsey

ABSTRACT

It has been shown that oxygen is required for the formation of a bond between iron and alumina whiskers. This oxygen may be introduced as naturally-occurring oxides on the surfaces of iron powder. Reinforcement has again been demonstrated in iron-alumina whisker composites subjected to short heating cycles. Evidence has been obtained that long heating cycles and excessive oxide content result in destructive attack on the alumina whiskers. Methods are projected for introducing the necessary oxygen by pretreating the whiskers.

TABLE OF CONTENTS

LIST OF TABLES

I. Introduction

This report describes research directed toward the development of high-strength composites of refractory metals and alumina whiskers. The work is sponsored by the Department of the Navy, Bureau of Naval Weapons.

A limited reinforcement of 80/20 nickel-chromium alloy and of pure iron by alumina (corundum) whiskers has been shown. It was found that an increase of 34% in the tensile strength of pure hydrogen-reduced iron could be achieved by the addition of 8 weight percent of alumina whiskers; 80/20 Ni/Cr showed an increase of 28% with 3.8 weight percent whiskers.

The purpose of the research program has been to obtain a detailed understanding of the process by which these metallurgical bonds were formed, in order to extend the reinforcement to higher levels and to a wider range of metals.

In the initial phase of the program, powdered metals, iron, 347 stainless steel and 80/20 Ni/Cr were melted on pure sintered alumina disks, to observe adhesion. It was found that the trivalent oxides tended to inhibit the formation of the necessary strong metallurgical bond. On the other hand, no bond could be formed without a small amount of oxygen present. To this end, iron was selected for intensive study.

The amount of oxygen needed to form a layer of iron spinel over the entire surface of the fiber was calculated to be 3.47×10^{-4} gram per gram fiber. If this amount of oxygen can be made available at the fiber surface, formation of the bond is possible. There are, however, three conditions defined

by experiment to date which must be met. These are:

(a) The fiber must be completely surrounded by metal, in contact with its surface, in the molten state.

(b) Oxygen must be made available at this interface.

(c) The resulting structure must be compatible with both iron and fiber, without destructive attack on the fiber itself.

Condition (a) means that the metal must in effect "wet" the fiber; and further, the fiber must be kept from floating out of the metal until the bond is formed.

Condition (b) may be met by the presence of dissolved oxygen in the metal, by the presence of metal or other oxides, or by transport through the molten surface of the metal.

Condition (c) implies a severely limited reaction of the fiber surface with oxygen and metal.

The present report is concerned with a series of four crucial experiments based on these hypotheses:

1. No significant interaction of iron and alumina whiskers can occur in the complete absence of oxygen.
2. Profound interaction between iron and whiskers results when the naturally-occurring iron oxides are present.
3. The interaction of iron oxides and alumina whiskers is temperature dependent.
4. The interaction of iron and alumina whiskers is time dependent.

To verify hypothesis (1) above, a layer of alumina whiskers was placed in a zircon boat, on top of a layer of iron powder. The boat was put in a tube

furnace, with an atmosphere of hydrogen and the temperature raised to 2900°F. After cooling in argon, the sample was visually and microscopically examined. The iron had formed a clean ingot below the fibers. The fibers were unchanged in appearance and there was no evidence of any interaction. The experiment was repeated, with a layer of fiber between the layers of iron powder. The result was the same: all the iron was found on the bottom of the boat, and no evidence of interaction could be found.

Samples were again prepared as above, and brought to melting indry hydrogen. At a temperature of 2850°F, a 97/3 volume percent mixture of argon and oxygen was then introduced into the furnace and held 10 minutes, after which cooling was done in argon. In the case of fibers placed on top of iron powder, the fibers were not wetted, but had taken on a brownish color. The iron had drawn up into droplets.

When the fiber was placed between two layers of iron, the fibers were deeply discolored, and there was evidence of attack by the iron oxide. The fibers were not included intact within the iron ingots, however, and the tensile strength of the iron (75,000 psi) showed no reinforcement. Notebook reference 881-27-b, c, d, e.

Two subsequent experiments further clarify the role of oxygen in the fiber-iron system. Intimate mixture of alumina whiskers and iron powder was prepared, with 15 weight percent whiskers on the total. These were treated in the following way: a boat containing the mixture and a second boat containing iron powder only were placed in a tube furnace, and the temperature raised to 1800°F in an atmosphere of dry hydrogen. Argon was then substituted for the hydrogen, and the furnace temperature was raised to 2800°F ± 20°F.

In one experiment, pure oxygen was added to the argon; in a second experiment, CO_2 was added. The results are given in Tables I and II.

Table I indicates the disastrous effect of excessive oxygen: with 10 $^{v}/_{o}$ the fibers and oxide were reduced to a brownish mass. There was no evidence of fiber retention. At lower oxygen levels, the metal appeared to be attached to the fiber as shot. These were separated magnetically from the loose whiskers and alumina content determined analytically. The high values proved to be illusory, however. The tensiles of the remelted materials showed no increase over the blank.

Table II shows the effect of very small amounts of oxygen, introduced as CO_2. There was little evidence of fiber retention; analytical data support this observation.

These experiments clearly show that without oxygen present, there is no interaction between iron and alumina whiskers. Earlier experiments had suggested this conclusion.

The use of the tube furnace requires that heating times be relatively long. In order to provide shorter cycles, a high-frequency induction furnace was put in operation. Atmospheres are contained within a transparant quartz envelope.

This equipment was used to investigate the infiltration of fiber by iron with its naturally-occurring oxides.

One gram of clean fiber was placed in the bottom of a high-temperature glass tube, and five grams of iron powder containing 6.4 $^{w}/_{o}$ oxygen was poured on top. This was put in a cylindrical graphite susceptor and set in the induction furnace. After purging with argon, the temperature was rapidly raised

TABLE I

EFFECT OF OXYGEN ON RETENTION OF ALUMINA WHISKERS IN IRON

Sample	w/o Fiber	v/o Oxygen in Argon	Result	w/o Al_2O_3 Retained
881-24-A	0	1.0	Good sample	---
881-24-B	15	1.0	Fibers black, metal beads.	17.09
881-24-C	0	5.0	Black glaze on metal.	---
881-24-D	15	5.0	Fibers black, metal beads.	11.2
881-25-A	0	10.0	Black-brown slag	---
881-25-B	15	10.0	Black brown slag	---

TABLE II

EFFECT OF OXYGEN AS CO_2 ON RETENTION OF ALUMINA WHISKERS IN IRON

Sample	$^{W}/_{o}$ Fiber	$^{V}/_{o}$ CO_2 in Argon	Result	$^{W}/_{o}$ Al_2O_3 Retained
881-17-A	0	0	No Wetting	---
881-17-B	15	0	No Wetting	0.135
881-17-C	15	5	Little Wetting	0.025
881-18-C	15	20	Some Slag	0.032

to 2800°F ± 20°F and held five minutes. There was no infiltration of the fiber by the molten iron. A series of experiments of this type is described in Table III.

The data indicate that, with the oxygen introduced as metal oxide, it is necessary that (a) the temperature be considerably higher than the melting point of the metal, and (b) that sufficient time be allowed for wetting and infiltration to take place. This experiment strongly suggests that the fibers may be destroyed rather than wetted. The appearance would be macroscopically the same. Metallurgical examination of the resulting pieces was not conclusive: intact large whiskers may be seen but the small wool-like filaments could not definitely be identified in the polished and etched surfaces.

A further experiment, using iron which had been heated in hydrogen to reduce the oxide content, is described in Table IV. Again the induction furnace was used. Little or no metal-fiber interaction could be seen. The metal flowed around the fibers, along the tube wall, leaving them essentially intact.

Since the reaction is time-dependent, a series of experiments to explore the effect of very short heating times was then undertaken. For this purpose, a vertical furnace with a hollow cylindrical silicon carbide heating element was used. This furnace may be brought to the desired temperature before the sample is introduced, which permits heating times limited only by the time required for the sample to reach thermal equilibrium.

Ten grams of iron powder containing 6.4 weight percent oxygen was mixed intimately with 0.8 grams of cleaned alumina whiskers. All casual aluminum metal was removed from the whiskers by alkali treatment. The mixture was placed in a dry high temperature glass tube, connected to a controlled pressure of

TABLE III

EFFECT OF TIME AND TEMPERATURE ON INTERACTION OF IRON POWDER AND Al_2O_3 FIBERS

Sample	Temperature (°F)	Time (Min.)	Result
886-19-2	2820	5	Melted ingot on top of fiber. No infiltration.
886-20-1	2980	0.1	No infiltration.
886-20-2	2980	0.5	Little infiltration.
886-20-3	2980	1.0	Little infiltration.
886-20-4	2980	2.0	Complete absorption of fiber.
886-19	2980	5.0	Complete absorption of fiber. Tensile 80,000 psi.

TABLE IV

EFFECT OF LOW OXIDE CONTENT ON WETTING OF Al_2O_3 BY IRON

Sample	Fiber Content (W/o)	Oxygen Content of Fe (W/o)	Temperature (°F)	Time (Min.)	Result
881-32-A	20	0.545	3000	12	Metal flowed past fibers.
881-32-B	20	0.545	3000	12	Same.
881-32-C	20	1.12	3000	12	Same.

20 mm Hg of argon. This tube was lowered into the vertical tube furnace preheated to 2900°F, and held two minutes. The resulting ingot showed no loose fibers. It was divided in two equal parts: one was held for tensile test; the other was returned to the furnace for an additional two minutes heating.

A third sample was similarly treated, except that a total heating time of six minutes was used. Blanks containing no fiber were treated in a similar way.

The technique for measuring tensile strengths has been improved by the development of a device for grinding an accurately round, smooth section of reduced diameter in the specimen. This method has eliminated clamp breaks entirely and materially improved the consistency of tensile data.

The tensiles on the above samples are given in Table V. In addition to the tensiles, microscope examination showed large fibers in the two minute sample, but no clearly defined small fibers. It is evident that the attack of the oxide on the fiber was minimal at the short time, with only the smallest whiskers destroyed. However, with longer heating times, the fibers were progressively destroyed, and the tensile strength reduced to that of the blank. An exploratory experiment using alumina whiskers which had been coated with nickel showed no beneficial effect from the coating. The coated fibers were by weight 70/30 Ni/Al_2O_3.

Fibers so coated were tightly packed in a mullite tube and heated to 2750°F in argon. The metal separated into small beads or shot, leaving the fibers clean.

In a second experiment, the coated fibers were mixed with Fe powder containing 0.54 $^{w}/_{o}$ oxygen as surface oxides, and heated to 2900°F in argon.

TABLE V

EFFECT OF TIME ON BONDING OF IRON AND ALUMINA WHISKERS

Sample	Fiber (W/o)	Temperature (°F)	Time (Min.)	Average Tensile (psi)
881-34-1	8	2900	2	117,000
881-37-1	8	2900	4	87,400
881-38-2	8	2900	6	86,500
881-34-2	0	2900	2	83,000

Again, the fibers were left clean, and the metal formed small shot scattered throughout.

In neither case was there evidence of useful metal-fiber interaction.

II. Discussion

There is no doubt that useful metallurgical bonds between metal and alumina whiskers can be formed. This has been demonstrated with 80/20 nickel/chromium alloy, and repeatedly with iron. To generate such bonds it is necessary that oxygen be present at the metal-alumina interface, while the metal is in the molten state. It is further necessary that the amount of oxygen be limited to that which will react to form a strong bond; excessive amounts of oxygen lead to eventual destructive attack on the whiskers.

The addition of the needed oxygen through the surface of the metal melt has not succeeded because the molten metal and the fiber do not form a true interface, but separate at once, leaving the condition that fiber must be surrounded by molten metal unsatisfied.

Two methods for assuring the presence of the proper amount of oxygen are now under investigation. One method is to use the naturally-occurring oxides on the iron powder in the formation of the bond, and then remove the excess oxygen by the addition of aluminum metal. This requires a careful sequence of short-time heating followed by rapid addition of the aluminum.

The second method now under investigation is that of adding oxygen to the whiskers in the form of oxides of the matrix metal. The metal oxide is generated from a metal-organic compound applied to the whiskers in solution. After drying, the fibers are heat-treated in the presence of a stoichiometric

amount of oxygen to decompose the metal-organic and generate the desired oxide *in situ*.

In the case of iron, ferrous acetate appears to satisfy the requirements, being water-soluble, and decomposing readily to permit the generation of FeO or Fe_2O_3, depending upon the amount of oxygen supplied.

This method has the advantage that the bond-former is associated with the whisker itself, and may be controlled under less stringent conditions than those of the actual metal melt.

Concurrently, an investigation of possible bonding materials other than oxygen has been started. Additionally, equipment for fusing metal *in vacuo* by induction is now operative, and should yield information with respect to the effect of adsorbed contaminants on bond formation.

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