HIGH TEMPERATURE OXIDATION STUDIES ON ALLOYS CONTAINING DISPERSED PHASE PARTICLES AND CLARIFICATION OF THE MECHANISM OF GROWTH OF SiO₂

Submitted to: Maj. Joseph W. Hager
Submitted by: G. Simkovich

August 1986

The Pennsylvania State University
University Park, Pennsylvania
THE PENNSYLVANIA STATE UNIVERSITY

College of Earth and Mineral Sciences

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A wide variety of high temperature oxidation tests have been conducted on Fe, Co and Ni based alloys. Results are discussed and several papers submitted for publication are appended.
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HIGH TEMPERATURE OXIDATION STUDIES ON ALLOYS CONTAINING DISPERSED PHASE PARTICLES AND CLARIFICATION OF THE MECHANISM OF GROWTH OF SiO₂

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Introduction

This report summarizes the work performed at The Pennsylvania State University during the period 15 Aug 1985 to 14 Aug 1986 under Grant No. AFOSR-85-0298. The project was directed by Prof. George Simkovich. Others that have contributed to the program are the following graduate students: C. Buss, D. H. Kim, B. Munn, S. W. Park, M. Y. Su and G. P. Wagner. Mr. Munn and Mr. Park have worked directly as 1/2 time research assistants on this grant while the other students have aided via interaction with Kim, Munn and Park or by aiding in the experimental program.

In this report we summarize the initial efforts on the project which includes the experimental arrangements and results obtained. Several papers that have been submitted for publication are included in this report as appendices.
Experimental Arrangement

In order to properly monitor the high temperature oxidation kinetics a thermal gravimetric analysis (TGA) system was constructed. This included a gas flowmeter system, furnace and a balance coupled to a computer to collect and partially analyze the data. Additional facilities utilized, e.g. optical microscopes, SEM, etc, were primarily in place.

The gas flowmeter system is capable of supplying to the reaction chamber a variety of gas mixtures. However, the oxidation experiments described in this report were all conducted at 1 atmosphere of oxygen since this represents a standard against which most materials are frequently measured.

The furnace assembly was constructed internally. It consists of a temperature controller and a furnace tube heated by SiC heating elements. As such this arrangement permits testing to at least 1400°C which is quite adequate for the needs of the project.

To obtain weight changes as a function of time a Cahn 1000 balance was purchased and was incorporated into the experimental arrangement. Finally, in respect to the apparatus, a computer set-up capable of handling the weight changes and a printer were assembled with the balance.

Oxidation Experiments

A relatively wide variety of oxidation tests were conducted on iron-based, cobalt-based and nickel-based alloys.

Typical of the iron-based results are those given in Appendix A which is a revised paper that has been submitted for publication in an AIME Symposium - "Alternate Alloying For Environmental Resistance". Basically, these tests were
conducted on alloys with various concentrations of the alloying elements chromium and/or silicon in the iron matrix with variable additions of Si$_3$N$_4$ particles. The Si$_3$N$_4$ particles dissolved to a major extent in the matrix material and also reacted with any oxygen present. Thus, the final alloy composition was iron + various levels of chromium + silicon at a number of levels + particles of unreacted Si$_3$N$_4$ and SiO$_2$.

Kinetic studies were made at a number of temperatures at about 1 atm of dry oxygen. It was found that the rates of oxidation were extremely slow and were comparable to many of the slowest growing commercial alloys. Optical microscopy, SEM and Kevex studies were also conducted on these alloys prior to and following the oxidation experiments. These studies revealed that the introduction of Si$_3$N$_4$ particles and their subsequent reaction with the matrix phase resulted in: (1) a lowering of the chromium content necessary to form a protective Cr$_2$O$_3$ layer; (2) altering diffusion in the protective layer(s) from primarily cationic to primarily anionic; (3) decreasing considerably the initial, non-parabolic weight gain; (4) decreasing the grain size of the growing scale; and, (5) the formation of a SiO$_2$ layer beneath the Cr$_2$O$_3$ layer.

Nickel and cobalt based alloys were also tested with additions of Si$_3$N$_4$ particles and were found to behave in a manner quite similar to that of the iron based alloys described above.

A small number of oxidation tests at 1000°C with 1 atm of O$_2$, were also made with additions of SiAlON, a high temperature compound found in the Si-Al-O-N system, to cobalt-chromium alloys. The particular SiAlON used in these studies was formed by sintering mixtures of Si$_3$N$_4$ (85 w/o), Al$_2$O$_3$ (10 w/o) and Y$_2$O$_3$ (5 w/o) at 1800°C in a nitrogen atmosphere. The Y$_2$O$_3$ is added to the SiAlON to aid densification during the sintering process.
The results obtained utilizing 10 v/o and 15 v/o of SiAlON are depicted in Figs. 1 and 2, respectively. Fig. 3 displays the weight gains per unit area of Co-Cr alloys at the same temperature and $P_{O_2}$ as that employed for the alloys with SiAlON additions. In comparing the results depicted in these figures it is seen that the particles and their dissolution products produce protective scales at concentrations of chromium between 10 to 12 wt%. Additionally, the weight gain per unit area for the better alloys containing SiAlON are significantly lower than those found in the binary Co-Cr system. Further work is underway on these alloys. In particular, scales developed and the alloy microstructures must be investigated.

The oxidation behavior of Ni-Cr-SiO$_2$ alloys has also been investigated. Appendix B is a copy of a paper that will be presented at the Univ. of Keele, England during the week of 1-5 Sept. 1986 at the Fourth International Conference on "Transport In Non-Stoichometric Compounds". Papers given at this meeting will be reviewed for publication in "Advances in Ceramics".

As may be seen from the contents of this paper the levels of concentrations of the dispersed phase SiO$_2$ were relatively high compared to most studies utilizing dispersions. In addition the size of the particles employed were extremely fine. The results obtained were quite encouraging in that the rates of oxidation were reduced considerably by the introduction of the SiO$_2$ particles while the chromium contents were at levels considerably less than conventional alloys.

A by-product of the use of high concentrations of a dispersed phase such as SiO$_2$ in these alloys is the decreased density of the alloy. Utilization of such alloys in systems where weight is important may well be considered as alternatives to conventional alloys.
The final effort described in this report relates to the electrical short
circuiting of SiO₂ layers growing on Si (or SiC or Si₃N₄). The initial thought
on this aspect was to utilize a noble metal as a wire embedded in the substrate
to be oxidized. Unfortunately, essentially all the noble metals react with Si to
form silicides or low melting eutectics. A search was and is being made of
oxides as possible probes. Such an oxide must not oxidize, must not react with
either Si or SiO₂ and should show appreciable electronic conductivity. At this
point it appears that Nb₂O₅ may be suitable as a non-interacting short
circuiting probe.
Figure 1. Isothermal oxidation curves for Co-Cr alloys with 10 vol. % SIALON at 1000°C in 1 atm. O₂.
Figure 2. Isothermal oxidation curves for Co-Cr alloys with 15 vol. % SiAlON at 1000°C in 1 atm. O₂.
Figure 3. Isothermal oxidation curves for binary Co-Cr alloys at 1000 °C in 1 atm. O₂.
APPENDIX A

"HIGH TEMPERATURE OXIDATION OF IRON BASED ALLOYS"

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Abstract

Iron-chromium alloys (0 to 14wt%Cr) with and without 10 vol % of Si$_3$N$_4$ particles, which were unstable in the matrix phase, were oxidized at 1173K and 1273K in 1 atm of oxygen. Oxidation of the iron-chromium alloys without the presence of Si$_3$N$_4$ revealed the following. The rate of oxidation decreased as the concentration of chromium was increased. An increase in temperature produced an increase in oxidation rate. Only pure iron showed FeO as a phase along with Fe$_2$O$_4$ and Fe$_3$O$_4$. As chromium was introduced a chromium spinel appeared as a product along with Cr$_2$O$_3$, Fe$_3$O$_4$ and Fe$_2$O$_3$. At higher chromium concentrations Fe$_2$O$_3$ was eliminated as a detectable product. Voids were present at the scale-alloy interface with Pt markers indicating considerable outward diffusion of cations during scale growth.

The initial addition of 10 vol % Si$_3$N$_4$, which dissolved extensively in the matrix phase, reduced considerably the rate of oxidation as compared to the nitride free materials. The appearance of an almost complete protective layer of Cr$_2$O$_3$ occurred at a quite low chromium concentration, about 5 wt %. Beneath the Cr$_2$O$_3$ layer SiO$_2$ formed to serve in further reducing the rates. It was found that the oxidation rate was relatively insensitive to temperature and that the scale was adherent during temperature cycling. Marker positions following oxidation of these alloys were at the gas - scale interface indicating inward diffusion of oxygen as the primary mode of transport during scale growth.

Revised prior to review and re-submitted for publication in TMS-AIME Symposium on "Alternate Alloying For Environmental Resistance"
Introduction

For high temperature oxidation resistance, a large number of iron based alloys, usually with high chromium contents, have been utilized to develop protective oxide scales. Systematic oxidation studies have been performed in some detail on the oxidation behaviour of binary Fe-Cr alloys (1-3). The oxidation rate of Fe-Cr alloys is reduced as chromium contents in the alloys are increased until about 20 weight percent after which the rate is not changed significantly with increased Cr content. The protective oxide scale formed on most binary Fe-Cr alloys are known to have, in general, poor scale adhesion to the underlying alloys probably due to void formation at the interface between oxide and alloy (4). It has been known that the presence of small amounts of oxides or nitrides such as ThO₂, Y₂O₃, or TiN in Ni-Cr and Fe-Cr alloys affects extensively the oxidation behaviour of such alloys (5-12). The oxidation rate is considerably decreased for alloys containing oxide or nitride dispersions and, additionally, scale adhesion to the underlying alloys is much improved. On the other hand, it is found that 1.29 weight percent of Li₂O in Ni-20Cr (7) and 1 percent SiO₂, TiO₂ or Cr₂O₃ in an Fe-20Cr alloys (6) have either little effect on the oxidation behaviour or increases the oxidation rates. Michels (7) has shown that increasing the amount of Y₂O₃ in Ni-20Cr alloys seems to increase the oxidation resistance although this author was not too concerned with such effects. A number of investigators have proposed several different kinds of models to explain the effects of oxide or nitride dispersions on oxidation behaviour (5-7) even though none of those proposed models have been well accepted as yet. There have been limited studies of the effects of stable oxide or nitride dispersions on iron based chromium containing alloys (6,9). Most of the previous studies have been limited to alloys with high chromium contents (14-20 weight %).

In the present investigation 10 vol% Si₃N₄ was added, prior to sintering, to a variety of Fe-Cr and Fe-Cr-Si alloys. The initial thought concerning this study was to have a silicon source in the Si₃N₄ particles available for growth of a protective scale of SiO₂. However, thermodynamic considerations indicated that a major portion, if not all, of the Si₃N₄ decomposes at the sintering temperature to give an Fe-Cr-Si alloy with some nitrogen in solution. SEM studies, Figure 1, revealed that some Si₃N₄ particles remained after sintering indicating that dissolution did not reach equilibrium. Although the Si₃N₄ particles are unstable in the matrix the oxidation tests proved to be very interesting and are discussed in the following sections.

Thermodynamics of Fe-Si System

The activity of silicon in the Si₃N₄ at 1500K, the sintering temperature in this study, is obtained from the free energy of formation of α-Si₃N₄ (13) assuming that P N₂ = 1 atm in this sintering operation. Thus, from

\[ \text{Si}(s) + \frac{2}{3} \text{N}_2(g) = \frac{1}{3} \text{Si}_3\text{N}_4(s) \quad \Delta G^0 = 389,100 + 198T(J) \]  (1)

one obtains a \( \gamma_{\text{Si}} = 6.204 \times 10^{-4} \) at 1500K. At equilibrium the activity in the alloy must equal the activity in the Si₃N₄. Use of the relation

\[ \ln \gamma_{\text{Si}} = \ln \gamma^0_{\text{Si}} + \chi_{\text{Si}} \frac{\gamma_{\text{Si}}}{\gamma_{\text{Si}}^0} \]  (2)

where \( \chi_{\text{Si}} \) is Wagner's self-interaction coefficient and literature values (14) of \( \gamma^0_{\text{Si}} = 3.00 \times 10^{-4} \) and \( \chi_{\text{Si}} = 14 \) at 1500K gives the relation...
Figure 1. Fracture surface topography of Fe-9Cr with an initial addition of 10\% Si$_3$N$_4$ (\# 2.89 Si) after sintering for 120 hours at 1500K; note remaining Si$_3$N$_4$ particles. A = Si$_3$N$_4$ particles B = matrix.

\[ \ln \gamma_{Si} = -8.113 + 14 N_{Si} \]  \hspace{1cm} (3)

Utilizing

\[ a_{Si} = \gamma_{Si} N_{Si} = 6.20 \times 10^{-4} \]  \hspace{1cm} (4)

and solving eqs. (3) and (4) for $N_{Si}$ gives $N_{Si} = 0.176$ in the alloy phase in equilibrium with $\alpha$-Si$_3$N$_4$. Assuming that all the silicon from 10 vol\% Si$_3$N$_4$ in an Fe-9Cr alloy dissolves into the alloy one obtains $N_{Si} = 0.055$. This is considerably below the value in equilibrium with Si$_3$N$_4$ indicating that the particles of Si$_3$N$_4$ should dissolve into the alloy for all the cases in this study.

The above analysis ignores the effects of chromium and nitrogen upon the activity of silicon. However, this is justified because $c_{Si}$ is relatively small (15) and because the concentration of nitrogen in the alloy is probably limited. Both chromium and nitrogen will tend to increase the activity of silicon in the alloy so that the mole fraction value of silicon calculated is probably somewhat greater than the actual equilibrium mole fraction.

Experimental

A series of alloys with and without an initial addition of 10 vol\% Si$_3$N$_4$ were made by conventional powder metallurgy methods. The starting materials were -100 mesh iron powder, -325 mesh chromium and silicon powder and $\alpha$-Si$_3$N$_4$ whose particle size ranges between 0.01 \( \mu \)m to 1 \( \mu \)m. The composition of the materials are listed in Table 1. The powders were mixed thoroughly, cold-pressed and then reduced at 1273K for 6 hours followed by a sinter at about 1500K in evacuated vycor or silica tubes for 96 to 120 hours. Alloys of Fe-Cr-Si were prepared in a similar fashion. The sintered samples were air quenched and were prepared for oxidation by grinding through 600 grit SiC abrasive paper and then were carefully washed and rinsed with acetone. Isothermal oxidation behaviour was measured by weight gain vs. time in about 1 atm of flowing oxygen on disc specimens approximately 1.2 cm in diameter x 0.2 cm in thickness. The samples were suspended with Pt wire from one arm of an automatic recording semi-micro balance (Ainsworth) in a Vycor reaction tube. Isothermal tests at 1173 and 1273K were conducted up to 80 hrs. When the oxidation test was started,
the sample was exposed to flowing oxygen and the test temperature was attained in about 3 min. No corrections for loss of weight due to nitrogen release was made since only a small amount of Si$_3$N$_4$ particles remained after sintering and were involved in the actual oxidation reaction.

Table 1 - Composition of the materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>C</th>
<th>O</th>
<th>Cl</th>
<th>S</th>
<th>Mo</th>
<th>Si</th>
<th>Fe</th>
<th>Si$_3$N$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al0008</td>
<td>0.015</td>
<td>0.016</td>
<td>0.01</td>
<td>Balance</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si$_3$N$_4$*</td>
<td>0.087</td>
<td>0.04</td>
<td>0.0097</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>99.97% purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* a content = 92.7%

Table 2 lists some of the alloys tested with additions of 10 vol% Si$_3$N$_4$. The resulting alloy compositions assuming that all of the Si$_3$N$_4$ dissolved into the matrix alloy are also listed. It is noted that the silicon content of such alloys is between 2.85 and 2.90 wt% Si.

Table 2 - The Concentration of Silicon in Alloys Assuming Complete Dissolution of the Initial Addition of Si$_3$N$_4$ Particles

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Total Silicon Content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
</tr>
<tr>
<td>Fe-10 vol% Si$_3$N$_4$</td>
<td>2.84</td>
</tr>
<tr>
<td>Fe-3Cr-10 vol% Si$_3$N$_4$</td>
<td>2.85</td>
</tr>
<tr>
<td>Fe-5Cr-10 vol% Si$_3$N$_4$</td>
<td>2.88</td>
</tr>
<tr>
<td>Fe-7Cr-10 vol% Si$_3$N$_4$</td>
<td>2.88</td>
</tr>
<tr>
<td>Fe-9Cr-10 vol% Si$_3$N$_4$</td>
<td>2.89</td>
</tr>
<tr>
<td>Fe-14Cr-10 vol% Si$_3$N$_4$</td>
<td>2.90</td>
</tr>
<tr>
<td>Fe-3Cr-2Si-10 vol% Si$_3$N$_4$</td>
<td>4.86</td>
</tr>
<tr>
<td>Fe-9Cr-2Si-10 vol% Si$_3$N$_4$</td>
<td>4.87</td>
</tr>
<tr>
<td>Fe-3Cr-1S1</td>
<td>1.00</td>
</tr>
<tr>
<td>Fe-3Cr-2S1</td>
<td>2.00</td>
</tr>
<tr>
<td>Fe-3Cr-3S1</td>
<td>3.00</td>
</tr>
<tr>
<td>Fe-9Cr-1S1</td>
<td>1.00</td>
</tr>
<tr>
<td>Fe-9Cr-2S1</td>
<td>2.00</td>
</tr>
<tr>
<td>Fe-9Cr-3S1</td>
<td>3.00</td>
</tr>
</tbody>
</table>

Upon the completion of kinetic measurements, the oxidized specimen was examined to evaluate surface topography by using the scanning electron microscope. Transverse sections of representative specimens were prepared by standard metallographic techniques and examined by optical microscopy and scanning electron microscopy. Some of the oxidized specimens were examined with a kevex-ray to evaluate the qualitative analysis of element distribution in the oxide scale. Standard x-ray diffraction techniques
were also employed for phase identification of the scales. Some of oxidized alloys which initially contained Si$_3$N$_4$ were heated after vacuum encapsulation in SiO$_2$ tubes at 1573 K and then held for 6 hours in order to transform the amorphous SiO$_2$ formed at the reaction temperature to a crystalline SiO$_2$ phase (cristobalite). Platinum marker experiments were conducted on Fe-29Cr alloys with and without 10 vol% Si$_3$N$_4$ to compare the oxide growth mechanisms on these alloys at 1273 K under 1 atm O$_2$.

**Results**

**Oxidation Kinetics**

Typical oxidation curves on Fe-Cr alloys, including pure Fe, with and without an initial 10 vol% Si$_3$N$_4$ (≈ 2.84 to 2.90 wt% Si), are plotted in Figures 2 to 5 as weight gain, in mg/cm$^2$, vs time, in hours, at 1173 K and 1273 K under 1 atm O$_2$. Figure 2 shows that the addition of Si$_3$N$_4$ reduces the oxidation rates significantly in comparison to that of pure Fe.

![Figure 2. Isothermal oxidation curves for pure Fe with and without an initial addition of 10% Si$_3$N$_4$ (≈ 2.84 Si) at 1173 and 1273 K.](image)

Similar behaviour is observed on the series of Fe-Cr alloys with again an initial 10 vol% Si$_3$N$_4$ (Figures 3 and 4). The incorporated Si$_3$N$_4$ reduces not only the oxidation rate but also the weight gain during the initial oxidation period even in an alloy containing only 3 weight percent of chromium. From these plots, it is seen that the major portion of the weight gain on all the Fe-Cr alloys with Si$_3$N$_4$ is essentially completed within the initial 20 hours of the oxidation period and also the oxidation rate is decreased with time, showing that a protective oxide scale forms. In addition, the oxidation behaviour of Fe-Cr alloys with Si$_3$N$_4$ additions exhibits little temperature dependence unlike that of the binary Fe-Cr alloys. Figure 5 shows the oxidation behaviour of the Fe-Cr alloys with an initial 10 vol% Si$_3$N$_4$ as a function of chromium content at 1273 K. A significant reduction in initial weight gain, which is completed within the initial 20 hours of oxidation, is seen as the chromium content in the alloys is increased until about 9 weight percent of chromium after which there is an increase in weight gain. Figure 6 shows two different weight gains, one after the first 20 hours and the other after 60 hours, plotted as a function of chromium content in the alloys containing initially Si$_3$N$_4$. From this plot, little difference between the two different weight gains is observed. This indicates that the formation of the protective scale is virtually completed within 20 hours in the Fe-Cr alloys with the introduction of silicon via the Si$_3$N$_4$ particles and in the presence of the un-reacted nitride particles.
Figure 3. Isothermal oxidation curves a) for Fe-3Cr alloys with and without and initial addition of 10 v/o Si$_3$N$_4$ (= 2.85 Si), b) for Fe-5Cr alloys with and without an initial addition of 10 v/o Si$_3$N$_4$ (= 2.88Si) in 1 atm O$_2$ at 1173K and 1273K.

Figure 4. Isothermal oxidation curves a) for Fe-9Cr alloys with and without an initial addition of 10 v/o Si$_3$N$_4$ (=2.89 Si), b) for Fe-14Cr alloys with and without an initial addition of 10 v/o Si$_3$N$_4$ (=2.90 Si).

A number of runs were also made on Fe-Cr-Si alloys. From plots of $(\Delta m/A)^2$ vs. time parabolic rate constants were calculated for these alloys and a few of the alloys containing the 10 vol% Si$_3$N$_4$ addition. The alloys and the derived parabolic rate constants are listed in Table 3. A number of factors are evident from the values listed in Table 3. Among these are the following. (1) Introduction of silicon directly to an Fe-Cr alloy decreases considerably the parabolic rate constants, except for the slightly anomalous behavior of the Fe-9Cr-1Si alloy. (2) The use of Si$_3$N$_4$ as a source of silicon dramatically reduces the parabolic rate constants of alloys of comparable silicon and low chromium contents. Thus, the effects produced by the use of Si$_3$N$_4$ particles are not fully explained by the resulting silicon contents indicating that the un-reacted particles and other factors may well affect the kinetics of reaction.
Figure 5. Isothermal oxidation curves for Fe-Cr alloys with an initial addition of 10 v/o Si₃N₄ as a function of Cr content in 1 atm O₂ at 1273 K.

Figure 6. Weight gain in Fe-Cr alloys with an initial addition of 10 v/o Si₃N₄ (see Table 2); one for initial 20 hours and the other for 60 hours in 1 atm O₂ at 1273 K.
Table 3 - Parabolic Rate Constants of Various Iron Based Alloys at 1273K - P₀₂ = 1 atm.

<table>
<thead>
<tr>
<th>Iron-Based Alloy Composition</th>
<th>Parabolic Constants ( g^2 \cdot cm^{-4} \cdot sec^{-1} \times 10^{14} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-3Cr</td>
<td>1,300,000.</td>
</tr>
<tr>
<td>Fe-3Cr-1Si</td>
<td>750,000.</td>
</tr>
<tr>
<td>Fe-3Cr-2Si</td>
<td>1,100.</td>
</tr>
<tr>
<td>Fe-3Cr-3Si</td>
<td>730.</td>
</tr>
<tr>
<td>Fe-3Cr-10 vol% Si₃N₄ (≈ 2.85 Si)</td>
<td>3.3</td>
</tr>
<tr>
<td>Fe-3Cr-2Si-10 vol% Si₃N₄ (≈ 4.86 Si)</td>
<td>0.55</td>
</tr>
<tr>
<td>Fe-9Cr</td>
<td>82,000.</td>
</tr>
<tr>
<td>Fe-9Cr-1Si</td>
<td>220,000.</td>
</tr>
<tr>
<td>Fe-9Cr-2Si</td>
<td>850.</td>
</tr>
<tr>
<td>Fe-9Cr-3Si</td>
<td>63.</td>
</tr>
<tr>
<td>Fe-9Cr-10 vol% Si₃N₄ (≈ 2.89 Si)</td>
<td>0.56</td>
</tr>
<tr>
<td>Fe-9Cr-2Si-10 vol% Si₃N₄ (≈ 4.87 Si)</td>
<td>290.</td>
</tr>
</tbody>
</table>

**Morphology**

Figure 7 shows the typical surface topography of pure iron, with and without the initial Si₃N₄ addition, after 50 hrs of oxidation at 1273 K. Fairly fine oxide grains and a smooth oxide surface are obtained on pure Fe with Si₃N₄ with a few oxide nodules, which are found in limited areas, while large oxide grains are observed on pure iron. Figure 7(c) and (d) show in more detail the oxidized surface of pure Fe with initial additions of Si₃N₄. There are only limited areas in which iron oxide overgrows the protective scale. Cross sections of regions of pure Fe, are seen in Figure 8. The thickness of oxide scale formed on pure Fe with initial additions of Si₃N₄ is significantly reduced while the thickness of oxide scale formed on pure Fe is considerable (several hundreds μm). Also, the oxide scale formed on pure Fe with Si₃N₄ is dense and has no void formation at the interface between metals and oxide. During cooling, after completing the kinetic measurement, neither significant spalling nor crack propagation of oxide is observed in pure Fe to which Si₃N₄ was added prior to sintering.

Figure 9 shows the surface topography of Fe-5Cr alloys, with and without initial Si₃N₄ additions, after 68 hours of oxidation at 1273 K. There is a significant difference between the oxide formed on these alloys. On the Fe-5Cr with the initial Si₃N₄ particles, the localized iron oxide occurs in limited areas only and the remaining portion of the surface is covered with a fine chromium oxide while on the Fe-5Cr alloy without Si₃N₄ only iron oxide is observed. The iron oxide formed on Fe-5Cr with the initial Si₃N₄ addition is localized to a few oxide nodules (Figure 9(b)). The cross sections of Fe-3Cr and Fe-5Cr alloys with the initial 10 vol% Si₃N₄, are shown in Figure 10. A thin and dense oxide scale, with some oxide nodules, is formed and pegged into the metal matrix without an internal oxidation zone.

Figure 11 shows the surface topography of Fe-9Cr with Si₃N₄ oxidized at 1173 K. The oxide over the entire region of the surface of the Fe-9Cr alloy with Si₃N₄ consists of essentially pure Cr₂O₃, while only iron oxide is formed on the surface of the Fe-9Cr alloy. It appears that the surface
oxide grooves on the chromium oxide lie parallel to the grinding grooves resulting from sample preparation. Similar features are observed in Fe-14Cr with an initial 10 vol% Si$_3$N$_4$ addition.

Figure 7. (a) Surface topography of pure Fe after 50 hours of oxidation at 1273 K; note the large iron oxide grains.

(b) Surface topography of Fe with an initial addition of 10 v/o Si$_3$N$_4$ (*2.284 Si) after 50 hours oxidation at 1273 K; a smooth iron oxide surface with oxide nodules.

(c) and (d) detailed view of (b): Showing (c) over-grown oxide and (d) fairly fine oxide grains.

Figure 12 shows the cross section of Fe-9Cr alloys oxidized for 50 hours at 1273 K. The internal oxidation zone with a thick external oxide scale is obvious in the binary Fe-9Cr alloy while thin and complex oxide scales are formed on the Fe-9Cr alloy with an initial 10 vol% Si$_3$N$_4$ additive. Figure 13(b) shows the concentration profile of elements in B area and Figure 13(c) in A area in Figure 13(a). These indicate that area B consists of essentially pure Cr$_2$O$_3$ while area A is primarily SiO$_2$.

Figure 14(b), shows that platinum markers initially placed on the alloy surface prior to oxidation are found on the top of the Cr$_2$O$_3$ formed on an Fe-9Cr alloy with Si$_3$N$_4$ after 50 hours of oxidation at 1273 K and the underlying Cr$_2$O$_3$ is seen in Fig. 14(a). On the other hand, the platinum marker is found in the middle of the oxide scale formed on an Fe-9Cr alloy
without Si₃N₄ after 72 hours oxidation at 1273 K (Figure 14(c)). This difference in marker position shows the change of oxide growth mechanism due to the incorporated silicon and remaining Si₃N₄ particles.

Figure 8. (a) Cross section of pure Fe after 50 hours oxidation at 1273 K; showing thick and porous iron oxide scale.

(b) Cross section of pure Fe with an initial addition of 10 v/o Si₃N₄ after 50 hours oxidation at 1273 K; showing relatively thick oxide nodule with thin oxide scale.

(c) detailed view of (b): the formed oxide scale in dense and pore free at the interface between metal and oxide

1: matrix  2: oxide scale  3: mounting material

It is noted that the figures presented in this section do not reveal the presence of any particles of Si₃N₄ remaining following the oxidation process. However, Figure 1 does show some nitride particles and additionally dissolution in acids of the alloys did give a residue whose x-ray patterns confirmed to α-Si₃N₄. Thus, the effects observed in these alloys must relate to both the silicon in the alloy as well as the un-reacted Si₃N₄ particles. The data in Table 3 already indicates that such must be the case.

X-ray Diffraction

Phase identification of the oxide scale was determined by X-ray diffraction analysis utilizing diffractometer and Debye-Sherrer.
Figure 9. Surface topography of Fe-5Cr alloys (a) without and (b) with an initial addition of 10 v/o Si$_3$N$_4$ (2.88Si) after 68 hours oxidation in 1 atm O$_2$ at 1273 K
1: Fe$_2$O$_3$  2. Cr$_2$O$_3$  3: Cr$_2$O$_3$/Fe$_2$O$_3$

Figure 10. Cross section of (a) Fe-3Cr alloy with an initial addition of 10 v/o Si$_3$N$_4$ (2.85Si) after 60 hours oxidation (b) Fe-5Cr alloy with an initial addition of 10 v/o Si$_3$N$_4$ (2.88Si) after 68 hours oxidation in 1 atm O$_2$ at 1273 K
1: matrix  2: SiO$_2$ scale  3: Fe$_2$O$_3$ formed as oxide nodule  4: electroplated Ni coating.

Figure 11. Surface topography of Fe-9Cr alloy with an initial addition of 10 v/o Si$_3$N$_4$ (2.89Si) after 70 hours oxidation at 1173 K showing the surface oxide grooves on the chromium oxide.
Figure 12. Cross section of (a) Fe-9Cr alloy after 48 hours oxidation at 1273 K (b) Fe-9Cr alloy with an initial addition of 10 v/o Si$_3$N$_4$ (*2.89Si) after 50 hours oxidation at 1273 K.

Figure 13. (a) Cross section of Fe-9Cr with an initial addition of 10 v/o Si$_3$N$_4$ (*2.89Si) after 50 hours oxidation at 1273K, (b) Concentration profile of elements in B showing high concentration of Cr; (c) Concentration profile of elements in area A showing high concentration of Si. 1: matrix, 2: oxide scale, 3: electroplated Ni coating.
techniques. Samples to be X-rayed were enclosed in evacuated SiO$_2$ tubes and held for 6 hours at 1573 K to crystallize the SiO$_2$ portion of the scale. After cooling, some of the oxide was detached, which was determined to be Cr$_2$O$_3$ and FeO, and the adhering oxides were determined to be SiO$_2$ with some Cr$_2$O$_3$. The oxides in Fe-Cr alloys with initial Si$_3$N$_4$ additions consisted of Fe$_2$O$_3$, Cr$_2$O$_3$, and SiO$_2$. The amounts of FeO decreased as the chromium content in the alloys was increased until no Fe$_2$O$_3$ was detected in the Fe-9Cr with Si$_3$N$_4$. In pure Fe with an initial addition of 10 vol% Si$_3$N$_4$, only FeO was detected. On the other hand, the oxides in binary Fe-Cr alloys without Si$_3$N$_4$ consisted of Fe$_2$O$_3$, Fe$_3$O$_4$, Cr$_2$O$_3$, and some Fe$_3$Cr$_2$O$_4$. FeO was not found in Fe-Cr alloys except for pure Fe. As the chromium content was increased, the ratio of Fe$_2$O$_3$/Fe$_3$O$_4$ increased and, in the Fe-14Cr, no Fe$_3$O$_4$ was detected in this study.

**Discussion**

For Fe-Cr alloys (including pure Fe) with an initial addition of 10 vol% Si$_3$N$_4$, the oxidation results show that the incorporated Si$_3$N$_4$ reduces the oxidation rate compared to binary Fe-Cr alloys without Si$_3$N$_4$ additions over the entire range of chromium content 1173 K and 1273 K under 1 atm O$_2$ (Figures 1 to 3).

In pure iron, the reduced oxidation rate appears to be due to the formation of SiO$_2$, resulting from the oxidation of the silicon and the Si$_3$N$_4$ particles since there is apparently a low iron diffusivity through the SiO$_2$ oxide scale. Further details of the formation of the SiO$_2$ layer will be discussed subsequently. A relatively thin oxide scale is formed with some thick oxide nodules in limited areas at 1273 K. These thick oxide nodules are not found at 1173 K. The thick oxide nodules might be formed due to the break away of the formed SiO$_2$ (16). Except for the oxide
nODULES, IT IS FOUND THAT THE OXIDE SCALE FORMED IS DENSE, PARTICULARLY AT THE INTERFACE BETWEEN METAL AND OXIDE, IN PURE Fe WITH AN INITIAL ADDITION OF $\text{Si}_3\text{N}_4$ WHILE VERY POROUS OXIDE IS FORMED WITH VOID FORMATION AT THE INTERFACE IN PURE Fe. ALSO, THE GRAIN SIZE OF OXIDE ON THE SURFACE OF PURE Fe WITH ADDITIONS OF 10 VOl% $\text{Si}_3\text{N}_4$ IS MUCH REDUCED EVEN IN THE OXIDE NODULES. THE DIFFERENCE BETWEEN THE FORMED OXIDE WITH AND WITHOUT $\text{Si}_3\text{N}_4$ PARTICLE ADDITIONS MAY BE DUE TO THE CHANGE OF THE OXIDATION MECHANISM.

IN THE Fe-Cr ALLOYS WITH INITIAL $\text{Si}_3\text{N}_4$ ADDITIONS SIMILAR RESULTS ARE OBSERVED IN OXIDATION BEHAVIOUR. IN PARTICULAR, IT IS FOUND THAT AN EXTERNAL, CONTINUOUS $\text{Cr}_2\text{O}_3$ LAYER IS DEVELOPED ON THE Fe-Cr ALLOYS WITH $\text{Si}_3\text{N}_4$ ADDITIONS INSTEAD OF AN EXTERNAL IRON OXIDE IN BINARY Fe-Cr ALLOYS NOT CONTAINING $\text{Si}_3\text{N}_4$. VERY THIN AND FINE GRAINED $\text{Cr}_2\text{O}_3$ SCALE, WITH ISOLATED OXIDE NODULES, IS FORMED ON Fe-3Cr AND Fe-5Cr ALLOYS WITH INITIAL $\text{Si}_3\text{N}_4$ ADDITIONS. THOSE ISOLATED OXIDE NODULES DO NOT FORM ON Fe-9Cr AND 14 Cr ALLOYS WITH THE $\text{Si}_3\text{N}_4$ ADDITIONS. IN PREVIOUS INVESTIGATIONS (8,9), IT WAS REPORTED THAT THE PRESENCE OF SMALL AMOUNTS OF STABLE OXIDE OR NITRIDE DISPERSIONS APPEARS TO REDUCE THE CRITICAL BULK CONCENTRATION OF CHROMIUM IN Fe AND Ni BASED CR CONTAINING ALLOYS NECESSARY TO FORM A CONTINUOUS, EXTERNAL $\text{Cr}_2\text{O}_3$ LAYER DURING OXIDATION. HOWEVER, THE PREVIOUS INVESTIGATIONS WERE LIMITED TO Ni AND Fe BASE ALLOYS WITH HIGH CHROMIUM CONTENT (14-20 WEIGHT %). HOWEVER, IN THE PRESENT INVESTIGATION, THE RESULTS INDICATE THAT THE CRITICAL BULK CONCENTRATION OF CHROMIUM NECESSARY TO FORM AN EXTERNAL CONTINUOUS $\text{Cr}_2\text{O}_3$ LAYER IS SIGNIFICANTLY REDUCED BY INCORPORATING SILICON VIA LARGE AMOUNTS OF PARTICLES OF $\text{Si}_3\text{N}_4$ IN ALLOYS PRIOR TO SINTERING.

THIS MAY BE A RESULT OF INCREASED NUCLEATION OF $\text{Cr}_2\text{O}_3$ ON THE REMAINING $\text{Si}_3\text{N}_4$ PARTICLES (OR FORMED $\text{SiO}_2$) WHICH PRODUCES A FINE GRAINED $\text{Cr}_2\text{O}_3$ THROUGH WHICH MOTION OF Fe IS SLOW AND UNDER WHICH $\text{SiO}_2$ LAYERS MAY FORM TO PROVIDE ADDITIONAL OXIDATION RESISTANCE. STRINGER (9) HAS SHOWN SIMILARLY THAT FINE GRAINED $\text{Cr}_2\text{O}_3$ FORMS ON ALLOYS CONTAINING OXIDE DISPERSIONS.

FROM THE OXIDATION CURVES IN FIGURE 2 TO 5 IT IS SEEN THAT, IN MOST OF THE Fe-Cr ALLOYS WITH $\text{Si}_3\text{N}_4$, THE OXIDATION RATES ARE DECREASED WITH TIME, SHOWING THAT THE OXIDE SCALES HAVE PROTECTIVE PROPERTIES. THIS IS DUE TO THE FORMATION OF PROTECTIVE $\text{Cr}_2\text{O}_3$/SiO$\text{$_2$}$ LAYERS RESULTING FROM OXIDATION OF THE CR CONTAINING ALLOY AND THE INCORPORATED SILICON AND THE REMAINING $\text{Si}_3\text{N}_4$. THE PROTECTIVE PROPERTIES OF THE SiO$\text{$_2$}$ SCALE IN THE Fe-Cr ALLOYS WITH $\text{Si}_3\text{N}_4$ MIGHT BE EXPLAINED BY THE MODEL OF BLOCKING LAYERS OF STABLE OXIDES IN OXIDE SCALES (5,17). HOWEVER, SUCH IS NOT THE CASE IN OUR ALLOYS SINCE MOST OF OUR ADDED PARTICLES REACTED UPON SINTERING TO PRODUCE ALLOYS CONTAINING SILICON IN SOLID SOLUTION WITH MINOR AMOUNTS OF UN-REACTIONED $\text{Si}_3\text{N}_4$ PARTICLES. NEVERMETHLESS, THESE COMPLEX ALLOYS DO CHANGE THE PATTERN OF GROWTH (FIGURE 13) FROM PREDOMINANTLY OUTWARD ION MOTION TO ANION MOTION INWARD. SUCH RESULTS FROM THE SILICON AVAILABLE TO FORM AN ALMOST COMPLETE SiO$\text{$_2$}$ LAYER UNDERLYING THE $\text{Cr}_2\text{O}_3$ LAYER (FIGURE 12).

THE VARIATION OF CHROMIUM CONTENT IN THE Fe-Cr ALLOYS CONTAINING INITIAL ADDITIONS $\text{Si}_3\text{N}_4$ GREATLY EFFECTS THE OXIDATION BEHAVIOUR. THESE RESULTS ARE ILLUSTRATED IN FIGURE 5. THE INITIAL WEIGHT GAIN IS GREATLY REDUCED AS THE CHROMIUM CONTENT IS INCREASED WHILE, AFTER THE INITIAL OXIDATION PERIOD, THE VARIATION OF CHROMIUM CONTENT IN THE ALLOY WITH INITIAL $\text{Si}_3\text{N}_4$ ADDITIONS DOES NOT MATERIALLY EFFECT FURTHER OXYGEN UP-TAKE (FIGURE 6). THE REDUCTION IN THE WEIGHT GAIN DURING THE INITIAL OXIDATION PERIOD IS ALSO DUE TO THE EARLY APPEARANCE OF EXTERNAL CHROMIUM OXIDE, WHICH ALSO LEADS TO THE REDUCTION OF THE AMOUNT OF IRON OXIDE FORMED.
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Reference

APPENDIX B

High Temperature Oxidation of Ni-Cr Alloys Containing a Dispersed Phase

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ABSTRACT

The oxidation behavior of Ni-Cr alloys (0-15 wt% Cr) with and without SiO$_2$ particles as a dispersion, whose amounts were varied from 5 to 40 volume percent, was studied at 1173K to 1373K in 1 atm of oxygen. The presence of SiO$_2$ as a dispersion in Ni-Cr alloys reduced considerably the oxidation rate as compared to the binary Ni-Cr alloys whereas the SiO$_2$ particles incorporated into pure Ni showed little effect on oxidation behavior. The oxidation rate of Ni-Cr alloys with SiO$_2$ particles as a dispersion phase showed a strong dependence on the inter-relation between volume percent of SiO$_2$ incorporated and chromium contents on the Ni-Cr alloys. The critical bulk concentration of chromium in the Ni-Cr alloys necessary to form an external, continuous Cr$_2$O$_3$ layer was significantly reduced by adding SiO$_2$ as a dispersion to the alloys. For Ni-Cr alloys containing SiO$_2$ particles, inward diffusion of oxygen ions was deduced to be responsible for oxide growth.
Introduction

Systematic oxidation studies have been well documented for binary Ni-Cr alloys, including pure Ni\textsuperscript{1-7}. Small additions of Cr to Ni increase the oxidation rate. The maximum oxidation rate is obtained at about 3-5 wt% Cr. With an increase in Cr content the oxidation rate then decreases due to Cr\textsubscript{2}O\textsubscript{3} and NiCr\textsubscript{2}O\textsubscript{4} blocking effects. Chromium additions of about 20 weight percent markedly reduce the oxidation rate due to formation of a continuous Cr\textsubscript{2}O\textsubscript{3} scale underneath an external NiO scale. Thus, for high temperature oxidation resistance, a large number of Ni based alloys, usually with about 20 weight percent of chromium contents, have been utilized to develop protective oxide scales.

It has been known that the presence of small amounts of oxides or nitrides such as ThO\textsubscript{2}, Y\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2} or TiN in Ni-Cr, Co-Cr and Fe-Cr alloys affects markedly the oxidation behavior of such alloys\textsuperscript{8-14}. The oxidation rate is considerably decreased for alloys containing oxides or nitrides and, additionally, scale adhesion to the underlying alloys is much improved. On the other hand, it is found that the addition of small amounts of Li\textsubscript{2}O or La\textsubscript{2}O\textsubscript{3} in Ni-20Cr alloys\textsuperscript{10} and SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and Cr\textsubscript{2}O\textsubscript{3} in Fe-20Cr alloys\textsuperscript{9} show either little effect on oxidation behavior or increased the oxidation rates. A number of investigators have proposed several different kinds of models to explain the effects of oxide or nitride dispersions on high temperature oxidation behavior\textsuperscript{8-11} although none of those proposed models have been universally accepted. Most of the previous studies have been limited to alloys with high chromium contents (14-20 weight percent) and with small amounts of an incorporated dispersion (2-5 volume percent).

In the present investigation, the effects of SiO\textsubscript{2} as a dispersed phase on the oxidation behavior of a number of Ni-Cr alloys are studied. There are three
distinctive approaches that differ from previous investigations: first, chromium contents in the Ni-Cr alloy with SiO$_2$ as a dispersion are varied, from 0 to 15 wt% Cr, to evaluate chromium content effects; secondly, unusually large amounts of SiO$_2$ particles are incorporated for the specific purpose of forming continuous protective SiO$_2$ scales; and, finally, the amount of SiO$_2$ as a dispersion incorporated into the Ni-Cr alloys is varied to evaluate the inter-relation between effects of chromium contents and volume percent of SiO$_2$ on the oxidation behavior.

**Experimental**

A series of alloys, with and without additions of SiO$_2$, were made by conventional powder metallurgy methods. The starting materials were 2-3 μm Ni powder, (99% purity), 2 μm chromium and amorphous SiO$_2$ (fumed silica) whose individual particle size ranges between 30 to 300 Å. The powders were mixed thoroughly, using a high speed blender and ball mill, and then were cold pressed. The cold pressed specimens were reduced in H$_2$ at 1273K for 6 hours followed by sintering at 1500K in evacuated vycor or silica tubes for 100 hours. The microstructures of a Ni-9Cr alloy, with and without 20 v/o SiO$_2$ particles, are shown in Fig. 1. The average grain size of Ni-9Cr alloys are shown in Figure 2 as a function of volume percent of incorporated SiO$_2$ particles. It appears that the grain size of the Ni-9Cr alloys with SiO$_2$ as a dispersion is significantly reduced as the volume percent of SiO$_2$ incorporated into the alloys is increased. The initially added amorphous SiO$_2$ was transformed to crystalline SiO$_2$ (cristobalite), which was detected by x-ray diffraction analysis, during the sintering procedure. The sintered samples were air quenched and were prepared for isothermal oxidation tests by grinding to 600 grit on silicon carbide abrasive paper and then were carefully washed and rinsed with acetone.
Isothermal oxidation behavior was measured by weight gain vs. time in about 1 atm of slow flowing oxygen on disc specimens 1.2 cm in diameter and 0.2 cm in thickness. The samples were suspended with Pt wire from one arm of an automatic recording semi-micro balance in a vycor reaction tube. Isothermal tests at 1173K, 1273K and 1373K were conducted up to 60 hours. When the oxidation test was started, the sample was exposed to flowing oxygen and heated to the test temperature in about 3 min. The weight gain measurements were not corrected for the formation of a gas phase resulting from the oxidation of Cr$_2$O$_3$ to gaseous CrO$_3$.

Upon completion of the kinetic measurement, the oxidized specimen was examined by scanning electron microscopy to evaluate surface topography. Transverse sections of representative specimens were prepared by standard metallographic techniques and examined by optical microscopy and scanning electron microscopy. Some of the oxidized specimens were examined with energy dispersive x-ray spectroscopy (E.D.S.) to evaluate elemental distribution in the oxide scale. Standard x-ray diffraction techniques were also employed for phase identification of the scales.

Results

Oxidation Kinetics

Typical oxidation curves on Ni-Cr alloys, including pure Ni, with and without SiO$_2$ dispersed particles, are plotted in Figures 3 to 7 as weight gain (mg/cm$^2$) versus time (hours) at 1173K to 1373K in 1 atm O$_2$. In Figure 3, the weight changes of pure Ni and Ni-3Cr alloys, with and without incorporated SiO$_2$ particles, at 1273K are shown. The addition of SiO$_2$ in pure Ni increased the initial oxidation rate after which the oxidation rates become quite similar during the steady state oxidation periods. Increased amounts of SiO$_2$ show
almost negligible effects on the oxidation behavior. On the other hand, the incorporated SiO\textsubscript{2} in Ni-3Cr alloys slightly reduces the oxidation rates both in the initial and the steady state periods of oxidation. The oxidation resistance is increased as the volume percent of SiO\textsubscript{2} in Ni-3Cr alloys is increased.

The effects, significant, of incorporated SiO\textsubscript{2} on the oxidation resistance of Ni-9Cr alloys are shown in Figure 4. The 5 volume percent of SiO\textsubscript{2} in the Ni-9Cr alloys increased the initial oxidation rates at 1273K and 1373K. After short periods of time, the oxidation rate is significantly reduced. Such seems to be due to the completion of a protective scale. Further addition of SiO\textsubscript{2} particles in the Ni-9Cr alloys reduced the oxidation rates systematically. As shown in Figure 4(b), sizable weight losses are obtained for Ni-9Cr alloys containing 10, 20 and 40 volume percent of SiO\textsubscript{2} during oxidation at 1373K.

Similar oxidation behavior is observed for both Ni-12Cr and Ni-15Cr alloys with SiO\textsubscript{2} as a dispersion, Figures 5 and 6. Again, weight losses are observed in all of the alloys containing SiO\textsubscript{2} as a dispersion during oxidation at 1373K. Such loss of weight is apparently due to the formation of the volatile oxide CrO\textsubscript{3}.

The weight changes obtained during oxidation of Ni-9Cr alloys with 10 and 20 volume percent of SiO\textsubscript{2} are plotted against time for temperatures from 1173K to 1373K in Figure 7. The initial weight gains of all of the alloys are decreased as the temperature is decreased. Furthermore, the differences in weight changes between Ni-9Cr-10 v/o SiO\textsubscript{2} and Ni-9Cr-20 v/o SiO\textsubscript{2} are significantly increased as the test temperature is increased.

In Figures 8a and 8b, the oxidation behavior of Ni-Cr alloys containing 20 volume percent of SiO\textsubscript{2} is replotted as a function of chromium contents at 1273K and 1373K respectively. The oxidation rates are dramatically reduced as the chromium contents are increased to 9 weight percent at 1273K. Further increase in the chromium content shows negligible effects on the oxidation behavior at
1273K. Similar behavior is obtained at 1373K but at a higher chromium content (12 weight percent).

**Morphology**

The surface topography of pure Ni, with and without SiO$_2$ particle additions, after 50 hours of oxidation at 1273K, is shown in Figure 9. Smaller grains of NiO for Ni-20 v/o SiO$_2$ in comparison to pure Ni are observed. Cross sections of pure Ni, with and without SiO$_2$, are shown in Figure 10. The oxide formed on Ni with 20 volume percent of SiO$_2$ are pegged into the metal matrix while the oxide formed on pure Ni shows a smooth interface.

A significant difference between the oxide topography on Ni-9Cr alloys, with and without 20 volume percent of SiO$_2$ addition, after 54 hours oxidation at 1273K, is shown in Figure 11. The oxide over the entire region of the surface of the Ni-9Cr-20 v/o SiO$_2$ alloy is primarily Cr$_2$O$_3$, while only NiO oxide is formed on the surface of the Ni-9Cr alloy. The surface topography of the Ni-9Cr-20 v/o SiO$_2$ alloy; after 64 hours oxidation at 1373K, is shown in Figure 12. The development of relatively large oxide nodules, which are mainly Cr$_2$O$_3$ and small amounts of NiO$_2$, are shown in Figure 12(a). The appearance of SiO$_2$ particles on the oxide surface are shown in Figure 12(b). Similar topographies of oxide surfaces are developed on the Ni-12Cr and Ni-15Cr alloy containing SiO$_2$. The cross sections of Ni-9Cr alloys, with and without SiO$_2$, oxidized for 60 hours at 1373K are shown in Figure 13. A thick and smooth oxide scale, mainly NiO, is formed on the Ni-9Cr alloy while a thin and complex oxide scale develops on the Ni-9Cr alloy with SiO$_2$. This latter scale is pegged into the metal matrix which additionally does not display an internal oxidation zone. Similar oxide scales are formed on the Ni-15Cr-10 v/o SiO$_2$ as shown in Figure 14.
The cross section of a Ni-12Cr alloy with 40 volume percent of SiO₂, oxidized for 60 hours at 1373K, is shown in Figure 15(a). Again a thin and complex oxide scale is developed. It is noted that SiO₂ particles are found in the Cr₂O₃ oxide, which is confirmed by the E.D.S. spectrum for Areas A shown in Figure 15(b). In Figure 15(b) and 15(c), the E.D.S. spectrums for Areas B and C are shown. From these spectrums one concludes that the main oxides formed on the Ni-9Cr-40 v/o SiO₂ are Cr₂O₃ and SiO₂.

X-ray Diffraction

Phase identification of the oxides formed during oxidation was determined by x-ray diffraction analysis utilizing diffractometer and Debye-Sherrer techniques. The oxides in Ni-Cr alloys consist of NiO and NiCr₂O₄ with some Cr₂O₃, which is only detected in the Ni-12Cr and Ni-15Cr alloys. In pure Ni with SiO₂ as a dispersion, the outer oxide scale consists mainly of NiO with some SiO₂ while the inner oxide consists of NiO, SiO₂ and Ni₂SiO₄. For the Ni-3Cr alloy with SiO₂, the outer oxide scale is mainly NiO and the inner oxide consists of Cr₂O₃, NiO, NiCr₂O₄ and SiO₂. Note that no Cr₂O₃ was detected on the binary Ni-3Cr alloy. In this study Cr₂O₃ and SiO₂ were always detected in Ni-Cr alloys containing SiO₂ particles. For Ni-9Cr alloys with SiO₂, the constituents of the oxide scale showed a strong dependency on the volume percent of incorporated SiO₂ and the temperature of oxidation. For Ni-9Cr alloys with low volume percents of SiO₂, x-ray diffraction analysis showed that the oxide scale for Ni-9Cr with SiO₂ consisted of NiO, Cr₂O₃, NiCr₂O₄ and SiO₂ (crystobalite) while the oxide scale for the binary Ni-9Cr alloy consisted of NiO and NiCr₂O₄. For Ni-9Cr-20 v/o SiO₂ alloy, no NiO was detected at 1273°K but at 1373K a small amount of NiO was found. No NiO was observed for Ni-9Cr with 40 volume percent of SiO₂ at either 1273K or 1373K. For the Ni-12Cr and
15Cr alloys with SiO$_2$ as a dispersion only Ni-12Cr alloy with 10 volume percent of SiO$_2$ showed the presence of NiO after oxidation at 1373K. A NiCr$_2$O$_4$ phase was always detected except for the Ni-12Cr and Ni-15Cr alloys with 40 volume percent of SiO$_2$.

Discussion

In pure nickel, the addition of SiO$_2$ as a dispersion does not significantly change the oxidation kinetics. Previous investigations\textsuperscript{15,16} on Ni with 2 weight percent of ThO$_2$ showed similar oxidation behavior except no increase in the initial oxidation rate of the ThO$_2$ containing alloys occurred. The increased initial oxidation rate in Ni with 10 and 20 volume SiO$_2$ may be due to the increased reaction areas for the initial oxidation period since the incorporated particles might be simply detached from the matrix during metallographic preparation for the oxidation test resulting from the poor adhesion between the metal matrix and the SiO$_2$ particles as shown in Figure 1(a). Furthermore the cavities, which were previously occupied by SiO$_2$ particles, might be underlain by other SiO$_2$ particles since the distance between the dispersed SiO$_2$ particles is small due to the incorporation of large amounts of SiO$_2$ into the pure Ni. Additionally, pores formed during sintering might be involved in this increase of initial area. By incorporating large amounts of SiO$_2$ particles into pure Ni, several effects on oxidation behavior are expected. The incorporated SiO$_2$ particles provide more grain boundary area as a result of the reduced grain size. Such boundaries provide a fast path for ion transport. Also, the particles reduce the cross sectional area available for ion transport. According to J. Stringer et al\textsuperscript{11}, dispersed particles in Ni-Cr alloy eliminate short circuit paths such as dislocations. Such reduces the oxidation rates since short circuit paths provide regions for rapid ion transport. Furthermore, NiO doped
with SiO\textsubscript{2} has an increased cation vacancy concentration, which increases the oxidation rate. However, the oxidation results show little differences between pure Ni with and without additions of SiO\textsubscript{2}. In view of the null effect of the SiO\textsubscript{2} particles in pure Ni one can only remark that whatever changes occur in the growth mechanism are such that they basically "balance out" to "no change" in the kinetics.

For Ni-Cr alloys containing SiO\textsubscript{2} as a dispersion, the oxidation results show that the presence of dispersed SiO\textsubscript{2} particles reduces the oxidation rate compared to binary Ni-Cr alloys over the entire range of chromium contents at temperatures from 1173K to 1373K (Figures 3 to 6). In Ni-3Cr alloys, the oxidation rates are gradually decreased as the volume percent of SiO\textsubscript{2} is increased. This seems to be due mainly to the formation of Cr\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} particles, which act as barriers for ion transport. However, a continuous Cr\textsubscript{2}O\textsubscript{3} scale or SiO\textsubscript{2} layer was not found as an inner oxide layer. It should be noted again that no Cr\textsubscript{2}O\textsubscript{3} was detected after oxidation of the binary Ni-3Cr alloy. The concentration of Cr\textsubscript{2}O\textsubscript{3} is increased as the volume percent of SiO\textsubscript{2} in the Ni-3Cr alloys is increased. Previous studies\textsuperscript{1,17} have indicated rapid diffusion of chromium along grain boundaries on fine-grained Ni-20Cr alloys. A similar behavior for Cr\textsubscript{2}O\textsubscript{3} formed in the Ni-3Cr alloy with SiO\textsubscript{2} as a dispersion might be considered since the incorporated SiO\textsubscript{2} in Ni-Cr alloys dramatically decreases the grain size as shown in Figure 2.

The significant effects of incorporated SiO\textsubscript{2} on the oxidation behavior of Ni based alloys containing intermediate amounts of Cr (9-15 weight percent) are shown in Figure 4 to 6. In particular, it is found that an external continuous Cr\textsubscript{2}O\textsubscript{3} layer is developed on all of the alloys with additions of SiO\textsubscript{2}. The formation of an external continuous Cr\textsubscript{2}O\textsubscript{3} scale has a strong relationship to the chromium contents and volume percent of SiO\textsubscript{2} in the Ni-Cr alloys. For Ni-9Cr
alloys with SiO₂, the alloy containing 40 volume percent of SiO₂ did not form NiO at 1373K. For Ni-12Cr alloys only the Ni-12Cr with an addition of 10 volume percent of SiO₂ formed NiO at 1373K. For Ni-15Cr alloys, none of the alloys showed the formation of NiO. On the other hand, spinel oxide (NiCr₂O₄) was always found for all of the Ni-Cr alloys with SiO₂ except Ni-12Cr and Ni-15Cr alloys with additions of 40 volume percent of SiO₂. Thus any NiO formed during the early stage of oxidation must eventually become converted to NiCr₂O₄ by reaction with Cr₂O₃. In previous studies ¹¹,¹⁴ it was reported that the presence of small amounts of stable oxides or nitride dispersions in Ni, Co or Fe based alloys with high chromium contents (16-20 weight %) appears to reduce the critical bulk chromium content necessary to form a continuous external Cr₂O₃ layer during oxidation. However, in the present investigation, the results indicate that the critical bulk concentration of chromium necessary to form an external continuous Cr₂O₃ layer is significantly reduced by incorporating large amounts of SiO₂. This might be explained by an initial selective oxidation of chromium due to rapid diffusion of chromium along grain boundaries since, as shown in Figure 2, the grain size of the alloy containing SiO₂ is dramatically reduced. Fleetwood ¹⁸ found that sub-grain boundaries in Ni-20Cr with 2ThO₂ are rapid diffusion paths for chromium. Additionally, according to Stringer et al ¹¹, stable, fine particles act as nucleation sites for Cr₂O₃ and help to form a continuous Cr₂O₃ layer at early stages of oxidation.

The weight loss shown to occur at 1373K oxidation of Ni-9Cr, Ni-12Cr, and Ni-15Cr alloys containing SiO₂ as a dispersion, Figure 4(b), 5(b), and 6, is due to the evaporation of chromium oxide through the reaction ¹⁹,²⁰.

\[ \text{Cr}_2\text{O}_3 \text{ (solid) + 3/2 } \text{O}_2 \text{ (gas) = 2CrO}_3 \text{ (gas)} \]
From the oxidation curves in Figures 4 to 7, it is seen that the oxidation rates of most of the Ni-Cr alloys containing SiO$_2$ particles are significantly reduced in comparison to the oxidation rates of the binary Ni-Cr alloys. The reduced oxidation rates are due to the formation of a continuous protective Cr$_2$O$_3$ layer resulting from selective oxidation of chromium in the alloys. In addition, the SiO$_2$ particles in the Cr$_2$O$_3$ layer, as shown in Figure 15(a), induce a further reduction in oxidation rates by decreasing the cross sectional area of Cr$_2$O$_3$ available for the transport of ions for oxidation and, according to J. Stringer and et. al.\textsuperscript{11}, by blocking the short circuit paths for rapid diffusion of chromium. Birchenall\textsuperscript{21} and Giggins and Pettit\textsuperscript{8} also suggest that stable oxide dispersions can act as diffusion barriers for outward motion of ions. Therefore, when an oxide grows normally by outward cation diffusion the presence of such stable oxides block the cation motion and inward diffusion of anions will occur. In the present investigation, the presence of the SiO$_2$ particles in the Cr$_2$O$_3$ layer, as shown in Figure 14 and 15, suggests that inward diffusion of oxygen ions (or atoms) is favored since the SiO$_2$ particles may be considered as inert markers.

Acknowledgements

We extend sincere thanks to the Metallurgy Program at Penn State and the Air Force Office of Scientific Research (Grant No. 85-0298) for their kind support of this study.
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Figure 15. (a) Cross section of Ni-12Cr alloy with 40 volume percent of SiO₂ oxidized at 1373K for 60 hours. E.D.S. spectrum for (b) Area A, (c) Area B, (d) Area C. 1 : Metal matrix 2 : Cr₂O₃ 3 : SiO₂ 4 : Bi.
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