HIGH TEMPERATURE GRAIN GROWTH AND OXIDATION OF Fe-29Ni-17Co (Kovar™) ALLOY LEADS*

J. J. Stephens, F. A. Greulich, and L. C. Beavis

Sandia National Laboratories
Albuquerque, NM 87185-5800

Abstract

One important application for the Fe-29Ni-17Co (Kovar™) alloy in wire form is in brazed feedthrough assemblies which are integral parts of vacuum electronic devices. Since Cu metal brazes are performed at process temperatures of about 1100°C, there is opportunity for significant grain growth to occur during the brazing operation. Additional high temperature exposure includes decarburization of the Fe-29Ni-17Co alloy wire in wet hydrogen for 30 min. at 1000°C prior to the Cu brazing operation. Two approaches have been used to characterize grain growth in two lots of Fe-29Ni-17Co alloy: (1) a "once-through" processing study to examine the effect of "one time only" device thermal processing on the resulting grain size, and (2) an isothermal grain growth study involving various times at 800-1100°C. The results of the "once through" processing study indicate that acceptable grain sizes are obtained from both cold worked and mill-annealed wire lots following Cu brazing. The isothermal grain growth study indicates that the linear intercept distance for Fe-29Ni-17Co can be described with a power law function of time, and that thermal exposure must be controlled at temperatures in excess of 900°C in order to avoid excessive grain growth.

A second study has characterized the oxidation kinetics of Fe-29Ni-17Co alloy wire in air at temperatures ranging from 550-700°C. The starting condition for this study included the "once through" decarburization and braze thermal processing steps described above. The results of this study indicate that the parabolic growth law applies for this material, and between 550 and 700°C, oxidation in this alloy occurs at an activation energy of 27.9 kcal/mole. This compares with an activation energy value of 21.9 kcal/mole when other oxidation data for this alloy at $\leq 700^\circ\text{C}$ are included. Other oxidation studies at higher temperatures ($\geq 750^\circ\text{C}$) indicate an activation energy of 52.2 kcal/mole for oxidation of Fe-29Ni-17Co alloy at temperatures greater than 790°C. Quantitative point analyses of the oxide scale formed at 600°C suggest that a significant fraction of the scale is close to the stoichiometry of the Fe₂O₃-type oxide. This is in contrast to previous studies of oxidation in Fe-29Ni-17Co alloy, conducted at the shorter times and higher temperatures which are typically used for glass sealing this alloy, where spinel-type oxides corresponding to (Fe,Ni,Co)₃O₄ constitute the majority of the oxide scale.

Note: Kovar™ and Ceramvar™ are registered trademarks of Carpenter Technology, Inc.

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Stephens/Greulich/Beavis

1

34

Introduction

The Fe-29Ni-17Co (Kovar™) alloy, in lead wire form, is often used in brazed electronic assemblies, including metal/ceramic vacuum electronic devices with bakeout temperature and pressure requirements which may exclude the use of silver base braze alloys. The primary advantage of using Fe-29Ni-17Co alloy in these brazed metal/ceramic joints is the good thermal expansion match of Fe-29Ni-17Co alloy to alumina ceramic at temperatures less than 450°C (1). In such applications, copper brazing is often utilized, and exposure to temperatures of about 1100°C can lead to significant amounts of grain growth in the Fe-29Ni-17Co alloy. It is interesting to note that both ASTM specifications for this alloy (F1466 for metal-to-ceramic sealing applications and F15 for glass-to-metal sealing applications) (2) do not explicitly require either cold-worked or mill-annealed wire product to be able to withstand specific thermal exposure(s) with a specific maximum grain size. Thus, it is generally incumbent upon the purchaser of Fe-29Ni-17Co alloy lead wire to determine the amount of grain growth which subsequent brazing-related thermal processing will cause.

The potential consequences of using Fe-29Ni-17Co alloy wire with a coarse "as-procured" grain size in a copper brazing application are illustrated in Figure 1. The wire sample shown in Figure 1b-c was the lead wire of an area-seal, which had been belt furnace-brazed into metallized alumina ceramic using a wet hydrogen atmosphere and a thermal process cycle consisting of 10 minutes above the melting point of copper (1084°C) with a peak temperature of 1109°C. Prior to the brazing operation, the lead wire had been subjected to a decarburization treatment consisting of 30 minutes at 1000°C in wet hydrogen. The lead wire fractured above the top of the copper braze fillet following bending involved with component electrical testing. Metallographic examination of "as-received" material from the same lot, shown in Figure 1a, revealed that the starting grain size, prior to decarburization and brazing, was equal to ASTM #3. The fractured lead wire, shown in Figure 1b-c, was found to have a grain size of ASTM #1-2, and the fracture path (see Figure 1c) appeared to go across a diametral section which contained about 4 grains. The coarse grain size thus appears to degrade the material's low cycle fatigue (or "lead fatigue") resistance. It was hypothesized that this lot of wire material was relatively coarse grained, due to a very high temperature anneal cycle ($\geq 1200^\circ\text{C}$) at a diameter $> 0.018"$, and was given a light finish draw to obtain the final diameter of 0.018": a non-uniform finish (i.e., where cold work is concentrated near the surface of the wire) draw could explain the existence of some fine grains close to the wire surface in the as-brazed condition shown in Figure 1b.

This paper presents a systematic study of the effect of high temperature exposure on the grain size of Fe-29Ni-17Co alloy wire. Two different lots of Fe-29Ni-17Co alloy were examined: Lot 1, with a diameter of 450 μm (0.018"), was purchased in the cold worked condition, while Lot 2, with a diameter of 500 μm (0.020"), was obtained in the mill annealed condition. Two types of thermal exposure were used for the grain growth study. The first type of thermal exposure examined the effect of a single decarburization cycle, braze thermal cycle, and subsequent air exposure at 600°C on the final grain size of both Lots of wire. This "once-through" processing study was designed to address the specific thermal conditions typically associated with Cu-brazed leads. The second type of thermal exposure consisted of evaluating the effect of varying lengths of time at 800°, 900°, 1000° and 1100°C on the final grain size of the wire. The latter study was intended to provide a predictive relation for intercept length/grain size as a function of time at temperature for this alloy.

The final part of this paper includes a study of the oxidation kinetics of Fe-29Ni-17Co alloy in air at temperatures ranging from 550-700°C. This temperature range was utilized in device production and was found to be outside the range of oxidation data for "modern" heats of Fe-29Ni-17Co alloy. The

Stephens/Grain/Braz 2 34

oxidation data obtained are also compared to the results of those previous oxidation studies.

Experimental Techniques

a. Materials Studied

The chemical composition of the two lots of Fe-29Ni-17Co alloy which were examined in this study are shown in Table 1. These analyses were provided by Allied-Signal Aerospace Co., Kansas City Division, and the various methods used are consistent with the chemical analysis techniques specified in ASTM F1466, "Standard Specification for Iron-Nickel-Cobalt Alloys for Metal to Ceramic Sealing Applications". The Inductively Coupled Argon Plasma technique combined with Emission Spectroscopy ("ICP" in Table 1) results were generated using a calibration Standard #160, procured from Brammer Standard Company, Inc., Houston, Texas. With respect to the critical oxide-forming elements which must be controlled, ICP is effective in measuring manganese, silicon, magnesium, zirconium and titanium. However, for the low levels of aluminum and chromium present, ICP is not a reliable technique. The Atomic Absorption technique ("AA" in Table 1) was used to generate compositions for manganese, aluminum and chromium. Note that while both ICP and AA give consistent results for manganese, different levels are obtained for aluminum and chromium. Finally, combustion analysis was used to measure carbon and sulphur for both lots of Fe-29Ni-17Co alloy. With respect to the chemical requirement for Fe-29Ni-17Co alloy shown in ASTM F1466, Lot 1 fully conforms, while Lot 2, which was procured in the early 1970's to conform to ASTM F15, is high in sulfur.

b. Grain Growth Studies

Two types of grain growth studies were performed: (1) a "once-through" processing study and (2) an isothermal annealing study. The former study was used to evaluate the amount of grain growth which the Fe-29Ni-17Co alloy would experience following all of the thermal processing involved in producing

Table 1. Chemical analysis (in wt.%) of the two lots of Fe-29Ni-17Co alloy wire studied. Data provided by Allied-Signal Aerospace, Kansas City Division. Where two numerical values are shown, they represent results obtained by the respective methods shown in the third column.

<u>Element</u>	<u>Lot 1</u>	<u>Lot 2</u>	<u>Method</u>
Fe	53.54	53.79	ICP
Ni	28.77	28.59	"
Co	17.17	17.02	"
Mn	0.26/0.26	0.20/0.21	ICP/AA
Si	0.048	0.061	ICP
Al	0.012/0.005	0.0095/0.002	ICP/AA
Mg	0.003	0.003	ICP
Zr	0.002	0.002	"
Ti	0.0016	0.0005	"
Cu	0.021	0.048	"
Cr	0.031/0.031	0.018/0.028	ICP/AA
Mo	0.021	0.017	ICP
P	0.001	<0.004	"
C	0.006	0.010	Combustion
S	0.001	0.010	"

stephens/Goodrich/Bentley 4 34

a Cu-braced lead in a specific component. The latter study was intended to examine the grain growth kinetics of Fe-29Ni-17Co alloy as a function of time and temperature. Both studies were performed using a Centorr model 17 tungsten element brazing furnace, in a wet hydrogen atmosphere. The heating and cooling profiles were designed in order to simulate the profiles which would be experienced in a belt-type brazing furnace.

The "once-through" processing study included the following thermal exposure: (1) a 30 minute hold at 1000°C, to simulate the decarburization and cleaning cycle, (2) ramp-up to either a "high temperature" braze cycle consisting of 10 minutes at 1109°C or a "low temperature" braze cycle consisting of 3 minutes at 1097°C and (3) air exposure at 600°C for a minimum of 10 hrs. Items 1 and 2 were run in the Centorr furnace in a wet hydrogen atmosphere, with heating and cooling profiles as indicated in Table 2. The final exposure (item 3) at 600°C was performed in a tube furnace, with all samples were air cooled, and was intended to simulate the final bakeout which this component received prior to "pinchoff" at the end of the manufacturing process.

The isothermal annealing study consisted of selected annealing times at the following temperatures: 800°, 900°, 1000° and 1100°C. Because of the slow grain growth kinetics at 800°C, relatively long times were required - up to 1800 minutes (30 hrs.) - to observe significant grain growth. By contrast, the exposures at 1100°C were much shorter, with minimum and maximum exposure times of 0.5 and 60 minutes, respectively.

c. Oxidation Studies

The starting material for the oxidation study consisted of wire samples which had been subjected to both the decarburization cycle and either the high or low temperature braze cycle of the "once-through" processing study. Wires from the various lots and conditions were cut to specific lengths, and were first weighed

Table 2. Description of heating and cooling cycles used for the "once through" processing study.

"High Temperature" braze cycle heating profile: (1) 15°C per min. to 1000°C. (2) hold 30 min. at 1000°C. (3) 10°C per min. to 1109°C. (4) hold 10 min. at 1109°C.

"Low Temperature" braze cycle heating profile: (1) 15°C per min. to 1000°C. (2) hold 30 min. at 1000°C. (3) 10°C per min. to 1097°C. (4) hold 10 min. at 1109°C.

Cooling Cycles for both types of runs were as follows:

Cooling Rate (°C/min.)	to a Temperature (°C) of:	Cooling Rate (°C/min.)	to a Temperature (°C) of:
25	1084	66	860
12	1075	80	800
13	1065	88	734
18	1051	81	673
19	1038	73	513
25	1019	55	472
35	993	50	397
50	956	25	50
61	910		

Stephens / Giech / Brall 5 34

using a Mettler model OMS balance, with a minimum resolution capability of 2 μ g. These samples were then hung across the span of an alumina boat, and inserted into a preheated box furnace which had been stabilized at the testing temperature (either 550°, 600°, 650° or 700°C). The samples were held in the box furnace for 20 hrs., at which time the power to the furnace was shut off, and the samples were allowed to furnace cool to <200°C before being removed from the furnace. The time required for the furnace to cool down to 200°C ranged from 4 to 5 hrs., depending on the testing temperature. The samples were then re-weighed, and subjected to nine additional furnace exposures, followed by re-weighing, for a total exposure time of 200 hrs at the test temperature.

d. Metallographic Procedures

Longitudinal metallographic specimens were used to evaluate the final grain size of each grain growth sample. Metallographic mounts measuring 1 inch in diameter were prepared by encapsulation of the Fe-29Ni-17Co alloy specimens in a low viscosity epoxy. The epoxy polymerization cycle consisted of a 16 hour hold at 33°C. The mounted samples were ground on 600 grit SiC paper then rough polished with 6 μ m diamond paste on nylon cloth. Polishing consisted of 1 μ m diamond paste on microcloth followed by two hours on a Vibromet with microcloth and a colloidal silica solution (pH=9). Etching was accomplished by submerging samples for approximately 20 seconds in to a fresh solution consisting of 1 ml Hydrofluoric Acid, 3 ml Hydrochloric Acid, 50 ml Nitric Acid and 150 ml acetic acid.

ASTM grain size numbers were obtained for all samples by direct comparison with a chart supplied by the Leitz Microscope Company, which was calibrated for use at 160x magnification with a flat etched specimen. For the isothermal annealing study, the distribution of intercept lengths were also measured to permit determination of the shape of the distribution along with the average intercept for a given sample. Digital photographs were obtained at calibrated magnifications of 196x and 778x, and test lines were drawn on those photographs following the procedures of ASTM E112. The individual intercept lengths were obtained using a Model ABD™ Digitizer digitizing tablet operated with a Macintosh IICx computer, using Digitize™ software (RockWare, Inc. Wheat Ridge, CO). A minimum number of 50 intercepts were obtained for each sample from Lots 1 and 2. The distribution of intercept lengths was found to be best characterized by the log-normal distribution (3,4). The lognormal median (μ) and variance (σ) of the intercept length were obtained for each sample using Statview II software.

Knoop microhardness data were obtained for samples in the "once-through" processing study. A minimum of five indents were obtained per sample, using a loading weight of 50 gm and a loading time of 15 seconds. We report the average hardness for each sample, along with the standard deviation of that measurement.

Results and Discussion - Grain Growth Studies

a. Once-Through Processing Study

Relative to the starting grain sizes of the two Lots of Fe-29Ni-17Co alloy, the ~1100°C braze cycles produce substantial grain growth. The effect on final grain size of the "once-through" processing cycle is shown in Figure 2 for Lot 1 material. Both high and low temperature braze processing conditions produce an ASTM grain size of 4-5, as shown in Tables 3 and 4. The results for Lot 2 material are shown in Figure 3. Relative to the Lot 1 material, the Lot 2

Stephany Grevich/Bratt

6

34

Figure 2 "Once through" processing study results for Fe-29Ni-17Co alloy. Lat 1 material. (a) As-received condition (cold worked material). (b) Following decarburization (30 min. at 1000°C) and "low temperature" braze thermal cycle (3 min. at 1097°C) in wet hydrogen, and 10 hr at 600°C in air. (c) Same processing sequence as (b) except a "high temperature" braze thermal cycle (10 min. at 1109°C) was used.

Figure 3 "Once through" processing study results for Fe-20%Ni-17Co alloy, Lot 2 material. (a) As-received condition (mill annealed material), ASTM #9. (b) Following decarburization (30 min. at 1000°C) and "low temperature" braze thermal cycle (3 min. at 1097°C) in wet hydrogen, and 10 hr. at 600°C in air. (c) Same processing sequence as (b) except a "high temperature" braze thermal cycle (10 min. at 1100°C) was used.

samples appeared to exhibit slightly finer grain sizes with the low and high temperature braze cycles producing ASTM grain sizes of 4.5 and 5 respectively. However, both lots of material exhibit final grain sizes which would be considered acceptable for use in several applications.

The microhardness and grain size data for various portions of lots 1001 and 1002 are shown in Tables 2 and 3. Within the context of reports regarding the three experiments, it appears that lots of 1001 appear to have little or no effect on either grain size or microhardness. That is the microhardness increases in microhardness for Lot 1 particularly in the longitudinal direction of longitudinal section and grain growth and grain size for both lots of 10 20% 15% is

Table 2 Grain size (ASTM Grain Size Number based on 100x images) and Knoop Microhardness results for the "once through" study using the high temperature braze thermal cycle.

Condition	ASTM GSN	Lot 1 Hardness (Knoop)	ASTM GSN	Lot 2 Hardness (Knoop)
1. As-Received	CW*	254 ±6.48	8-9	168 ±9.93
2. 30 min 1000°C "decarb" + 10 min 1100°C wet H ₂ "Braze"	4-5	143 ±1.94	4-5	150 ±9.88
3. Condition 2 + 10 hr/600°C - air	4-5	158 ±5.92	6	155 ±6.23
4. Condition 2 + 20 hr/600°C - air	4-5	146 ±2.75	5-6	173 ±6.20
5. Condition 2 + 100 hr/600°C - air	4	141 ±2.63	4	149 ±5.89
6. Condition 2 + 200 hr/600°C - air	5	155 ±9.97	6	141 ±4.35

Table 4 Grain size (ASTM Grain Size Number, based on 160x images) and Knoop Microhardness results for the "once through" study using the low temperature braze thermal cycle.

Condition	ASTM GSN	Lot 1 Hardness (Knoop)	ASTM GSN	Lot 2 Hardness (Knoop)
1. As-Received	CW*	254 ±6.48	8-9	161 ±9.93
2. 30 min 1000°C "decarb" + 3 min. 1097°C wet H ₂ "Braze"	4-5	156 ±1.00	5	154 ±2.05
3. Condition 2 + 10 hr/600°C - air	4-5	153 ±3.87	5-6	148 ±2.87
4. Condition 2 + 20 hr/600°C - air	5	167 ±13.4	6	159 ±6.48
5. Condition 2 + 100 hr/600°C - air	5	151 ±3.07	5-6	149 ±5.33
6. Condition 2 + 200 hr/600°C - air	5-6	140 ±5.67	6	139 ±3.82

* Heavily cold worked, fine grained structure.

Stephen / Gerold / Braze 9 34

...by the same order of 1000 and 1000 respectively. For the case of Lot 2, while there is no clear trend in microstructural change, it does appear that 1000 and 1000 exposures maintain the finest grain size. These observations maintained the isothermal grain growth experiments discussed in the following section.

For a number of the conditions shown in Tables 3 and 4, the Lot 2 material exhibits slightly finer grain sizes than Lot 1 material. Two possible reasons may account for these differences: (1) there might be a greater density of grain growth inhibitors such as inclusions in Lot 2, or (2) a substantially larger driving force for grain growth exists in the cold worked Lot 1 material. The former reason is probably more likely since certain samples of Lot 2 did seem to contain more inclusions than were observed in Lot 1 also. With respect to the latter reason, we are unable to quantify the differences in the starting conditions since we do not know the exact cold working process conditions used for Lot 1 or the mill annealing temperatures used for Lot 2 material.

2. Isothermal Annealing Study

The isothermal annealing study represents an attempt to examine the grain growth kinetics of Fe-20Ni-17Cu alloy using single time and temperature values for each sample. However, since we included all the data generated in have engineering utility, finite heating and cooling times were involved, similar to those shown in Table 2 for the 'once through' processing study. The numerical results obtained for Lots 1 and 2 are shown in Tables 5 and 6, respectively. The data show that, for both lots of Fe-20Ni-17Cu alloy, that substantial amounts of grain growth occur in reasonable times (measured in minutes rather than hours) at 900°C and higher temperatures. However, for a given set of times at a particular temperature (eg., 900°, 1000° or 1100°C), the dominant variable appears to be peak temperature, rather than time at temperature. This dominance of temperature is a result of the fact that samples were subjected to realistic furnace heating and cooldown cycles, rather than being quenched from the peak temperature. These results are generally consistent with the results of Park (5), who studied the grain size of Kovar as a function of temperature, and found that increases in temperature were more effective than time in promoting grain growth.

Qualitative Observations

The isothermal annealing results for Lot 1 (cold worked) material following selected times at 900°C are shown in Figure 4. While 20 minutes at 900°C is clearly enough time to recrystallize to a fine grain size (see Figure 4a), much longer times - eg., 180 or 600 minutes at 900°C, as shown in Figures 4b and 4c - have caused substantial amounts of grain growth. The results for Lot 1 at 1100°C are shown in Figure 5, and suggest that recrystallization and grain growth are very rapid at this temperature. The tabulated results for Lot 1 at 1100°C (see Table 5) indicate that longer times do lead to additional grain growth, but that the majority of grain growth has occurred after relatively short times at 1100°C. The results for Lot 2 material at 1100°C, shown in Figure 6, are consistent with the Lot 1 results, except that time at temperature seems to have more effect on grain growth for Lot 2 at these temperatures.

Quantitative Observations

In order to quantify the amount of grain growth for a given process time and temperature, we obtained the distribution of intercept lengths using the methods described above, and attempted to fit the data to both the normal and log-normal distributions. We found that the log-normal distribution,

Figure 10-34

Table 2 Summary of the intercept length distribution results generated for Lot 1 Fe-20Ni-17C alloy in the isothermal annealing study. The μ and σ are the mean and standard deviation of the lognormal distribution for a particular sample. μ and σ are calculated from μ and σ for a given sample using eqs. 2a and 2b.

Sample ID	Time (minutes)	Temperature (°C)	Sample Population	μ (μm)	σ (μm)
H1A	60	800	110	9.74	2.02
H2A	60	800	98	6.21	1.80
H3A	180	800	109	7.41	1.66
H4A	600	800	149	11.27	1.93
H5A	1800	800	145	11.10	2.03
H6A	20	900	171	9.87	1.67
H7A	60	900	93	16.85	2.07
H8A	180	900	79	19.96	1.99
H9A	600	900	69	20.78	2.33
H10A	6	1000	78	19.50	2.05
H11A	20	1000	152	28.27	1.69
H12A	60	1000	85	29.25	1.93
H13A	180	1000	68	40.99	1.72
H14-2C	0.5	1100	163	28.09	1.70
H15-2C	2	1100	85	32.68	1.79
H16C	6	1100	82	34.72	1.74
H2C	20	1100	90	36.95	1.78
H17C	60	1100	73	48.30	1.70

Table 3 Summary of the intercept length distribution results generated for Lot 2 Fe-20Ni-17C alloy in the isothermal annealing study.

Sample ID	Time (minutes)	Temperature (°C)	Sample Population	μ (μm)	σ (μm)
AR-Lot 2			110	9.74	2.02
H3C	60	800	98	6.21	1.80
H4C	180	800	109	7.41	1.66
H5C	600	800	149	11.27	1.93
H1C	1800	800	145	11.10	2.03
H6C	20	900	171	9.87	1.67
H7C	60	900	93	16.85	2.07
H8C	180	900	79	19.96	1.99
H9C	600	900	69	20.78	2.33
H10C	6	1000	78	19.50	2.05
H11C	20	1000	152	28.27	1.69
H12C	60	1000	85	29.25	1.93
H13C	180	1000	68	40.99	1.72
H14-2C	0.5	1100	163	28.09	1.70
H15-2C	2	1100	85	32.68	1.79
H16C	6	1100	82	34.72	1.74
H2C	20	1100	90	36.95	1.78
H17C	60	1100	73	48.30	1.70

Stephens/Grosholz/Grosholz 11 34

 

Figure 5 Results for isothermal grain growth study at 1100°C. Fe-29Ni-17Co alloy, Lot 1 material. All anneals were performed in wet hydrogen, with belt furnace cooldown profile. (a) 2 minutes at 1100°C. (b) 20 minutes at 1100°C. (c) 60 minutes at 1100°C. (note: see Fig. 2a for as-received Lot 1 microstructure.)

Figure 6 Results for isothermal grain growth study at 1100°C. Fe-29Ni-17Co alloy, Lot 2 material. All anneals were performed in wet hydrogen, with belt furnace cool-down profile. (a) 2 minutes at 1100°C. (b) 20 minutes at 1100°C. (c) 60 minutes at 1100°C. (note: see Fig. 3a for as-received Lot 2 microstructure.)

$$N(x (\mu m)) = \frac{1}{(2 \pi)^{0.5} x \ln \sigma} \exp[-0.5*((\ln x - \ln \mu)/\ln \sigma)^2] \quad (1)$$

where x is the intercept length, μ is the geometric mean and σ is the variance of the distribution, produced the best fit to the data from both lots of material. This is consistent with many other investigators who have characterized normal grain growth (3). Examples of the appropriateness of the log-normal distribution are shown in Figure 7, where the distribution of intercept lengths for various Lot 2 samples are plotted using logarithmic probability paper. Figure 7a compares the as-received condition to data obtained for samples which were annealed for 20 minutes at 900°, 1000° and 1100°C, while Figure 7b compares the as-received sample to samples annealed for 60 minutes at the four temperatures investigated. In every case, a straight-line fit to the data appears to be appropriate - which, on the logarithmic probability paper, denotes the log-normal distribution.

The resulting values of μ and σ for the various isothermal annealing study samples are shown in Tables 5 and 6. For a given sample condition, generally finer intercept lengths are obtained with the Lot 2 samples (mill annealed material), relative to the Lot 1 (cold-worked) samples. This general trend is shown in Figure 8, where the intercept lengths for Lot 1 and 2 samples subjected to 20 minute anneals at 900° and 1100°C are illustrated. The finer grain size for Lot 2, relative to Lot 1, is more apparent following higher temperature anneals, as is shown for the 20 minutes at 1100°C condition in Figure 8. As indicated above, we cannot conclusively explain the differences between the Lots 1 and 2 results because we do not know exact details of the prior processing history for both Lots of material.

In order to generate predictive relations for the intercept length distributions as a function of time and temperature, it is necessary to first calculate the first and second moments of the log-normal distribution. The first moment, herein denoted $\langle L \rangle$, represents the expected mean intercept length for a given sample condition, while the second moment ($\langle L^2 \rangle$) is related to the skewness of the data (6). The two moments of interest are obtained as follows:

$$1st \text{ moment} = \langle L \rangle (\mu m) = \exp [\ln \mu + 0.5 (\ln^2 \sigma)] \quad (2)$$

$$2nd \text{ moment} = \langle L^2 \rangle (\mu m)^2 = \exp [2 \ln \mu + 2 (\ln^2 \sigma)] \quad (3)$$

We found that relatively simple power law equations incorporating both a time and temperature variable best characterized the data. This formulation, as well as other formulations which were examined for the Lot 2 data, are described in the following sections.

Simple Power-Law Correlations for Mean Intercept Length $\langle L \rangle$, and the Second Moment, $\langle L^2 \rangle$

The data for $\langle L \rangle$ and $\langle L^2 \rangle$, calculated from the values of μ and σ shown in Tables 5 and 6 for Lots 1 and 2, respectively, were analyzed using multivariable linear regression techniques and the following empirical power law equations:

$$\langle L \rangle (\mu m) = A [t (\text{minutes})]^n \exp(-Q/RT) \quad (4a)$$

Stephens/Greulich/Berens

15

34

Figure 7 Distribution of intercept lengths shown for isothermal anneals performed in wet hydrogen. Fe-29Ni-17Co alloy, Lot 2 material. (a) 20 minute anneals. (b) 60 minute anneals. Note that a straight line fit on this cumulative-log plot - equivalent to a log-normal distribution - would be a reasonable approximation for each data set.

$$\langle L^2 \rangle (\mu\text{m})^2 = A' [t (\text{minutes})]^{n'} \exp(-Q'/RT) \quad (4b)$$

where A (units of $\mu\text{m}(\text{minutes})^{-n}$) or A' ($\mu\text{m}^2(\text{minutes})^{-n'}$), n or n' and Q or Q' (both in kcal/mole) are constants obtained from the regression analysis. The results of the regression analysis for $\langle L \rangle$ and $\langle L^2 \rangle$ are shown in Tables 7 and 8, respectively. The results for both Lots 1 and 2 exhibit reasonably good fits to the data, as evidenced by the values of r^2 which range from 0.92 to 0.95. For both Lots 1 and 2, the relatively low values of the time exponent do confirm the results of the qualitative analysis - i.e. that maximum process temperature dominates the total time at temperature in determining the final distribution of intercept lengths and/or grain size for the Fe-29Ni-17Co alloy. However, it is important to note that time also plays an important role, as shown in Figures 9 and 10 for Lots 1 and 2 respectively. The data and correlations given by eq. 4a for the mean intercept length ($\langle L \rangle$) do suggest that times at temperatures $\geq 900^\circ\text{C}$ need to be controlled to avoid excessive grain growth in the Fe-29Ni-17Co alloy.

The question of whether or not the long time results at 1000°C and all data obtained at 1100°C are affected by the impingement of grains with the surface of the wire should be considered. Beck (7) and co-workers demonstrated in the late 1940's that, for sheet material, the slope of the log-log plot of mean grain diameter vs. time is no longer linear, and approaches the thickness of the sample after long periods of time. Beck (7) also indicated that this same effect is observed for wires - with the bamboo structure as the limiting case. It would appear, however, that attainment of the bamboo structure in wires would be expected only after very long periods of time. Recent modeling of the inhibition of grain growth in wires of single phase metals or alloys at large grain sizes (8) suggests that the transition from a "surface independent" or bulk growth rate to the asymptotic behavior discussed by Beck ought to occur when the mean grain diameter is approximately 2/3 of the wire diameter. In an effort to demonstrate that impingement of the surface is *not* an issue in the current

Table 7. Results of regression analysis for the first moment of the log-normal distribution of intercept lengths, $\langle L \rangle$ (μm), using the power law relation shown in eq. (4a).

<u>Material</u>	<u>A</u> ($\mu\text{m} (\text{minutes})^{-n}$)	<u>n</u>	<u>Q (kcal/mole)</u>	<u>r²</u>
Lot 1	1.79E5	0.138	22.521	0.947
Lot 2	5.44E5	0.176	20.332	0.949

Table 8. Results of regression analysis for the second moment of the log-normal distribution of intercept lengths, $\langle L^2 \rangle$ (μm^2), using the power law relation shown in eq. (4b).

<u>Material</u>	<u>A'</u> ($\mu\text{m}^2(\text{minutes})^{-n'}$)	<u>n'</u>	<u>Q' (kcal/mole)</u>	<u>r²</u>
Lot 1	4.99E10	0.289	45.352	0.940
Lot 2	4.13E9	0.381	40.800	0.920

Stephens/Greville/Beavis 17 34

Figure 8 Comparison of intercept lengths for Fe-29Ni-17Co alloy Lots 1 and 2 material, for the isothermal anneals consisting of 20 minutes at 900°C and 1100°C, respectively.

data set, we examined a number of alternative grain growth formulations - including one which accounts for a maximum grain size. Since all of these alternative grain growth correlations include starting grain size as a parameter, we were forced to limit this survey to the data for Lot 2 only.

Power Law Correlations for $\langle L \rangle$ Without Impingement

The simplest models which account for the original grain size (8) are those which subtract the square of the initial mean intercept length, $\langle L_0 \rangle^2$, from the square of the final mean intercept length, $\langle L \rangle^2$:

$$\langle L \rangle^2 - \langle L_0 \rangle^2 = A [t \text{ (minutes)}] \exp(-Q/RT) \quad (5)$$

where A, and Q are constants obtained from linear regression analysis. We have examined a generalized form of eq. 5, as follows:

$$\langle L \rangle^m - \langle L_0 \rangle^m = A [t \text{ (minutes)}]^n \exp(-Q/RT) \quad (6)$$

where A, n and Q are constants obtained from multivariable linear regression analysis and m is equal to 1, 2, or 3. The results obtained for the data from Lot 2 material, with $\langle L_0 \rangle$ equal to 7.33 μm , are shown in Table 9. Note that none of these correlations have a quality of fit parameter, r^2 , which approaches the results obtained for Lot 2 with the simple power law relation given in eq. 4a. A plot of the case for $m=2$ in comparison with the Lot 2 data (not shown) indicated a reasonable fit to the data except for the short time data at 800°C and longer time data at 1100°C - at both extremes, the $m=2$ correlation given in Table 9 overestimates the value of $\langle L \rangle$. While it is possible that the effects of

Figure 9 Comparison of data and regression analysis results for isothermal annealing study performed on Fe-29Ni-17Co alloy, Lot 1 material. (a) Mean intercept length (equivalent to the first moment of the log-normal distribution) as a function of time and temperature. (b) Second moment of the log-normal distribution.

Figure 10 Comparison of data and regression analysis results for isothermal annealing study performed on Fe-29Ni-17Co alloy, Lot 2 material. (a) Mean intercept length (equivalent to the first moment of the log-normal distribution) as a function of time and temperature. (b) Second moment of the log-normal distribution.

20 34

Table 9. Results of regression analysis using the mean intercept length ($\langle L \rangle$) data for Lot 2 with initial grain size taken into account. The measured initial intercept length, equal to 7.33 μm was used for $\langle L_0 \rangle$, along with eq. 6.

m	A ($\mu\text{m}^m(\text{minutes})^{-n}$)	n	Q (kcal/mole)	r ²
1	1.97E9	0.501	50.593	0.730
2	1.80E13	0.629	65.433	0.810
3	2.86E17	0.773	82.222	0.861

impingement account for the discrepancy at 1100°C, it is not clear why the m=2 correlation overestimates the value of $\langle L \rangle$ following relatively short times at 800°C.

Accounting for Impingement Effects: The Burke Equation

We also examined whether the particular approach for dealing with the inhibition of grain growth processes by means of the impingement of the sample surface developed by Burke (9, 10), could better describe the data obtained for the Lot 2 material. Burke's original equation, which includes both a term for initial mean intercept length, $\langle L_0 \rangle$, and maximum attainable mean intercept length, termed herein $\langle L_{ult} \rangle$, can be written as follows:

$$\langle L_{ult} \rangle (\langle L_0 \rangle - \langle L \rangle) + \langle L_{ult} \rangle^2 \ln \frac{(\langle L_{ult} \rangle - \langle L_0 \rangle)}{(\langle L_{ult} \rangle - \langle L \rangle)} = A [t (\text{min})] \exp(-Q/RT) \quad (7)$$

We have evaluated the use of a modified Burke equation, which incorporates a time exponent, n:

$$\langle L_{ult} \rangle (\langle L_0 \rangle - \langle L \rangle) + \langle L_{ult} \rangle^2 \ln \frac{(\langle L_{ult} \rangle - \langle L_0 \rangle)}{(\langle L_{ult} \rangle - \langle L \rangle)} = A [t(\text{min})]^n \exp(-Q/RT) \quad (8)$$

The data for Lot 2 were evaluated using eq. 8 and various iterative values of $\langle L_{ult} \rangle$ ranging from 256 μm down to 56 μm , in order to maximize the correlation coefficient, r². We found that the highest correlation coefficient was obtained with a value of $\langle L_{ult} \rangle$ equal to 56 μm , as follows:

$$56(7.33 - \langle L \rangle) + (56)^2 \ln \frac{(56 - 7.33)}{(56 - \langle L \rangle)} = 3.16 \times 10^{15} [t(\text{min})]^{0.787} \exp(-79,701/RT)$$

with a correlation coefficient (r²) equal to 0.887. While this is a better fit to the Lot 2 data than was obtained with the power law equation corrected for original grain size, i.e. eq. 6, it clearly is not as good a fit to the Lot 2 data as was obtained with the empirical power law equation given by eq. 4a. Based on these additional results, we feel comfortable in proposing that the time/temperature combinations observed in the isothermal grain growth study are not significantly affected by impingement with the surface of the wire.

Results and Discussion- Oxidation of Fe-29Ni-17Co Alloy

a. Weight Gain As a Function of Time and Temperature

Stephens / Greulich / Brown 21 34

In general, parabolic or quasi-parabolic oxidation kinetics were observed for all of the oxidation samples run. Plots of normalized weight gain as a function of time at temperature for samples subjected to the high temperature "once-through" processing study are shown in Figure 11, along with results for the low temperature "once-through" samples for Lot 2 material, plotted in Figure 12. For all three of these sets of oxidation samples, the data at the various times and temperatures were fit to the following kinetic equation for the normalized weight gain, $\Delta W(\text{gm/cm}^2)$:

$$\Delta W(\text{gm/cm}^2) = B(\text{time}(\text{hr}))^n \exp(-Q_{\text{app}}/RT) \quad (9)$$

where $B(\text{gm-hr}^{-n}/\text{cm}^2)$, n , and $Q_{\text{app}}(\text{kcal/mole})$ are constants obtained from the results of the multivariable linear regression analysis. Note that the *apparent* activation energy for oxidation, Q_{app} , is one half of the activation energy for oxidation, Q , which is proportional to the square of the normalized weight gain, and is used later in this section. The numerical results obtained using eq. 9 are shown in Table 10. All of these results indicate that time exponents close to 1/2 (i.e. ideal parabolic behavior) are obtained. The individual data correlations shown in Table 10 are plotted in comparison with the data in Figures 11 and 12. They indicate reasonably good agreement with the experimental data, as is reflected in the high values of r^2 shown in Table 10. Table 10 also includes the results of an analysis obtained using eq. 9 for all of the oxidation runs for Lots 1 and 2, which resulted in a time exponent of 0.550 and a value of Q_{app} equal to 13.941 kcal/mole. The observation of parabolic oxidation behavior in Fe-29Ni-17Co alloy is consistent with the previous results of Pask (5), Piscitelli, et. al. (11) and Abendroth (12). The last entry in Table 10 is a "cumulative fit" which also includes data for six runs for Fe-27Ni-25Co (CeramvarTM) alloy (13) that were run in parallel with the Fe-29Ni-17Co alloy 550-700°C oxidation experiments. This "cumulative fit" obtained a time exponent (n) equal to 0.537, with an apparent activation energy (Q_{app}) of 13.262 kcal/mole. It suggests that the oxidation behavior of the Fe-27Ni-25Co alloy is very similar to the results discussed herein for the Fe-29Ni-17Co alloy.

Table 10. Results of regression analysis for oxidation of Fe-29Ni-17Co alloy using eq. 9. "High" and "Low" denote wet hydrogen pretreatments of 30 minutes at 1000°C followed by either 10 minutes at 1109°C or 3 minutes at 1097°C, respectively. Note that the correlation for "all data" also includes oxidation data for one Lot 1 sample pre-treated with the "Low" once-through processing cycle. Finally, "All data + Fe-27Ni-25Co" includes six 200 hr. runs conducted on the Fe-27Ni-25Co alloy (CeramvarTM alloy) over the temperature range 550-700°C.

<u>Lot/Condition</u>	<u>B</u> (gm-(hr) ⁻ⁿ /cm ²)	<u>n</u>	<u>Q_{app} (kcal/mole)</u>	<u>r²</u>
1/High (4 runs)	0.7701	0.600	15.105	0.970
2/High (4 runs)	1.3372	0.551	15.972	0.949
2/Low (3 runs)	0.1401	0.471	10.987	0.984
All data (12 runs)	0.4812	0.550	13.941	0.931
All data + Fe-27Ni-25Co	0.3488	0.537	13.262	0.940

Stephens/Greulich/Beavis

22

34

Figure 11 Weight gain as a function of time and temperature for Fe-29Ni-17Co alloy. Starting condition: high temperature braze cycle used for the "once-through" processing study. (a) Lot 1 material. (b) Lot 2 material.

Stephens/Grevlich/Boris

23

34

Figure 12 Weight gain as a function of time and temperature for Fe-29Ni-17Co alloy, Lot 2 material. Starting condition: low temperature braze cycle used for the "once-through" processing study.

The oxide scales obtained from transverse metallographic cross sections of the "once-through" process study samples aged in air, and air cooled, for 10, 20, 100 and 200 hrs. at 600°C, were compared to the final scale obtained in the oxidation study samples at 600°C. Figures 13 and 14 shows these results for Lots 1 and 2 samples, originally subjected to the high temperature "once-through" pre-treatment, respectively. The 10 hr. samples in Figures 13a and 14a suggest that a uniform oxide scale is not established until longer times, e.g. approximately 20 hrs. The longer time samples exhibit reasonably compact external oxide scales, along with some limited amount of internal oxidation, occurring, presumably, along grain boundaries. The scales for both Lots 1 and 2 show at least two distinct types of scale: a medium gray scale is generally observed next to the base material, along with a lighter-gray phase encountered closer to the external surface of the sample. It is also interesting to note that the relative fraction of medium and lighter gray phases in the scale appears to be different for the samples which were air cooled (Figures 13 a-d and 14a-d) relative to the weight-gain samples, which were always furnace cooled to avoid spallation of the oxide scale (Figures 13e and 14e).

To further investigate the different phases contained in the oxide scale, both calibrated X-ray elemental maps and quantitative point analyses were obtained on the Lot 2 low temperature braze cycle oxidation sample (see Figure 14d) which was run in air for 200 hrs. continuously at 600°C. The calibrated X-ray maps, shown in Figure 15, indicate a number of interesting features: (a) the near-surface Fe-29Ni-17Co alloy is apparently enriched in Ni, Co and very slightly in Mn, while quite depleted in Fe; (b) the innermost oxide scale appears to be predominantly Fe-rich, along with with some Ni, Co and Mn; (c) the bulk and central part of the scale is dominated by Fe-rich oxide; (d) close to the external surface, the scale is composed of both Fe- and Co- rich scale.

Stephany/Greulich/Bennis

24 34

Figure 13 Transverse metallographic cross sections showing the evolution of oxide scale thickness at 600°C for Fe-29Ni-17Co alloy, Lot 1 material. Starting condition: high temperature braze cycle used for the "once-through" processing study. (a) 10 hrs., furnace cool. (b) 20 hrs., air cool. (c) 100 hrs., air cool. (d) 200 hrs., air cool. (e) weight gain sample, 10 x 20 hrs., furnace cool.

↔
20 μm

↔
20 μm

Figure 14 Transverse metallographic cross sections showing the evolution of oxide scale thickness at 600°C for Fe-29Ni-17Co alloy, Lot 2 material. Starting condition: low temperature braze cycle used for the "once-through" processing study. (a) 10 hrs., furnace cool. (b) 20 hrs., air cool. (c) 100 hrs., air cool. (d) 200 hrs., air cool. (e) weight gain sample, 10 x 20 hrs., furnace cool.

Figure 15 (see next page) Qualitative X-ray maps of a sample from Lot 2 which was subjected to the low temperature braze process cycle, followed by 200 hrs. in air at 600°C. All maps obtained using K_{α} lines. (a) Fe map, obtained at a level of 100 wt.%. (b) Ni map, obtained at a level of 30 wt.%. (c) Co map, obtained at a level of 20 wt.%. (d) Mn map, obtained at a level of 2 wt.%. In each photograph, the top arrow denotes the metal/oxide scale interface, while the lower arrow indicates the oxide scale/air interface.

Figure 16 contains higher magnification photos of the same sample in both secondary electron and backscattered electron modes. The backscattered image, Figure 16b shows the locations of points where quantitative wavelength dispersive analyses were performed, and also indicates that there is very little atomic number contrast throughout the entire oxide scale. Lack of atomic number contrast is to be expected since the four metallic elements contained in significant quantities in Fe-29Ni-17Co alloy (ie., Fe, Ni, Co and Mn) are nearest neighbors on the periodic table. The results of the quantitative point analyses, included in the caption of Figure 16, are consistent with the results of the X-ray maps shown in Figure 15. Thus, the innermost scale (point a) consists of primarily of oxide with Fe as the metallic atom, along with a limited amount of Ni and Co. The amount of Fe in the scale increases in the middle part of the scale, as evidenced by points c and d - although there are also some spots (see point d) where there is a measurable amount of Co present. Finally, the outermost portion of the scale - typified by point b - contains a significant amount of Co in the scale. The observation of Co as concentrated in the outer part of the scale suggests that at 600°C Co has somewhat higher mobility than Fe, and substantially higher mobility than Ni, in the oxide lattice. This inference is based on the observations of Barstow, et. al. (14), who investigated the preferential segregation of Co towards the scale-gas interface resulting from oxidation of various binary Ni-Co alloys at 1000°C. However, the high temperature oxidation results with binary alloys of Co-Fe and Ni-Fe are somewhat at variance to the present results. Piscitelli, et. al. (11) indicate that one would expect higher cation diffusivities for Fe relative to Co at 1200°C, and for Fe relative to Ni at 1000°C, in oxidation of binary Co-Fe and Ni-Fe alloys, respectively. Clearly, the substantial difference in temperature between the present study and these binary oxidation studies preclude more detailed comparisons.

While we have not performed x-ray diffraction analysis on the oxide scales, the point analysis results obtained (see Figure 16) suggest that for the mid-scale region (i.e. points a and d in Figure 16), that the stoichiometry of the oxide scale is predominantly a Fe_2O_3 type oxide, since the at.% O levels observed are closer to the 60 at.% O in Fe_2O_3 rather than the 57.14 at.% O which would be found with a pure Fe_3O_4 spinel-type oxide. However, the Co-rich region typified by point b in Figure 16, with 58.32 at.% O measured, suggests that a mixed $(Fe, Ni, Co)_3O_4$ spinel-type oxide would dominate on the outer portion of the scale. Finally, the results on the inner scale, typified by point a, which measured 58.90 at.% O, suggest that a mixture of both types of oxides are present in this region.

Two of the previously cited studies of the oxidation of Fe-29Ni-17Co alloy (11, 12) have utilized x-ray diffraction to characterize the structure of their scales. Both of these previous studies found that the oxide scale found on Fe-29Ni-17Co - at temperatures higher than investigated here - consist of a cubic oxide (either the spinels Fe_3O_4 or $(Fe, Ni, Co)_3O_4$) along with with small amounts of $\alpha-Fe_2O_3$. Piscitelli, et. al. (11) observed that the amount of $\alpha-Fe_2O_3$ increased at long times and lower temperatures. The high temperature x-ray work done by Abendroth (12) indicates that only the spinel phase is present, and he concludes

Stephens/Greulich/Brown

27

34

100% Fe map

30% Ni map

20% Co map

2% Mn map

Figure 16 Secondary and Backscattered electron micrographs showing the location of quantitative point analyses performed at various locations in the oxide scale. Same sample as described in Figure 15. (a) Secondary electron image. (b) Backscattered electron image. Quantitative analysis of the four points a-d (in at.%), based on the average of three adjacent points, are as follows:

Point	Si	Cr	Mn	Fe	Co	Ni	O
a	0.017	0.009	0.026	37.330	1.611	2.109	58.898
b	0.007	0.014	0.012	34.588	6.997	0.058	58.324
c	0.002	0.008	0.010	40.328	0.036	0.014	59.602
d	0.022	0.004	0.054	38.148	2.634	0.045	59.093

that the α -Fe₂O₃ present is the result of oxidation at lower temperatures. All of the oxidation results cited here are consistent with the binary Fe-O phase diagram (15), which shows Fe₂O₃ and Fe₃O₄ in equilibrium with each other over a broad range of O contents, with Fe₃O₄ having a wider range of stoichiometry - and thus dominating the two-phase region between these phases - at temperatures in excess of 1000°C.

It is important to note (see ref. 12) that the spinel-type oxide (Fe,Ni,Co)₃O₄ is the more adherent oxide to the Fe-29Ni-17Co alloy, and that pre-oxidation treatments of this alloy for glass-to-metal sealing applications need to be designed so that this oxide forms exclusively. Abendroth (12) found that this can be best achieved by oxidizing Fe-29Ni-17Co alloy in dry air at 850-1000°C, followed by application of the glass to the oxidized surface while the alloy is still at red heat. He also suggests that if the glassing operation is performed following cooling of the pre-oxidized alloy, that the reheating should be performed under inert gas blanket to avoid formation of α -Fe₂O₃. Those interested in glass-to-metal sealing of Fe-29Ni-17Co are directed to the discussions of sealing techniques in Kohl (16) and decarburization treatments by Notis (17).

Correlations for Parabolic Oxidation of Fe-29Ni-17Co Alloy Between 550° and 1100°C

This section will examine the effect of temperature on the parabolic oxidation kinetics for Fe-29Ni-17Co alloy. We will include the data obtained in the present study, along with the data from previous studies by Pask (5), Piscitelli, et. al. (11) and Abendroth (12). It should be emphasized from the outset that, as in the case of grain growth, the times studied at the highest temperatures were as short as 0.1 hr. (5), while the lower temperature oxidation data in the present study were obtained over times up to 200 hrs. Because each study has observed parabolic oxidation kinetics for this material, the data presented in the previous sections have been analyzed using the following parabolic kinetic equation:

$$(\text{Norm. Wt. Gain})^2 (\text{gm}^2/\text{cm}^4) = C (\text{time}(\text{hrs})) \exp(-Q/RT) \quad (10)$$

where the constant C (gm²/cm⁴-hr) and the activation energy for oxidation, Q (kcal/mole), are obtained from regression analysis. As noted earlier, for a given data set, Q will have roughly twice the value of Q_{app}, since the latter quantity (see eq. 9) is related to the first power of the normalized weight gain.

By applying eq. 10 to the same data sets as shown in Table 10, we have obtained the parabolic kinetic results shown in Table 11. While it should be noted that the use of eq. 9 gives generally higher correlation coefficients (r²) for the various data sets than eq. 10, the values of r² are still quite high. In order to compare the data from the various studies, we define the parabolic rate constant, k², as

$$k^2 (\text{gm}^2/\text{cm}^4\text{-hr}) = (\text{Norm. Wt. Gain})^2/\text{Time}(\text{hrs}) = C \exp(-Q/RT) \quad (11).$$

We have plotted the values of k² from the present study, and the other referenced studies, in Figure 17. Close examination of this data plot suggested that there were two different temperature regimes for the oxidation of the Fe-29Ni-17Co alloy: at higher temperatures, from 1/T=0.0007 up to about 1/T=0.00095 (ie., 1100° down to 780°C), there appeared to be a regime with a high activation energy, while at lower temperatures (less than 780°C) there

Stephens/Garlick/Beavis 30 34

Table 11. Results of analysis using the parabolic growth equation, , eq. 10. The same data sets as defined in Table 10 are listed. (Note that because eq. 10 relates time to $(\Delta W)^2$, entries for Q will be about two times that of the entries for Q_{app} shown in Table 10.)

Lot/Condition	$\underline{C}$ ($\text{gm}^2\text{-hr/cm}^4$)	$\underline{Q}$ (kcal/mole)	r^2
1/High (4 runs)	1.4586	30.208	0.936
2/High (4 runs)	2.8400	31.943	0.924
2/Low (3 runs)	0.0152	21.978	0.956
All data (12 runs)	0.3638	27.880	0.889
All data + Fe-27Ni-25Co	0.1726	26.553	0.906

Figure 17 Comparison of the oxidation results for Fe-29Ni-17Co alloy obtained in this study with those of other investigators (5, 11, 12). Parabolic kinetics ($n=0.5$) were assumed to construct this graph. Note that there is a transition at approximately 790°C ($1/K \sim 0.00094$) from the high temperature oxidation regime, with the activation energy equal to 52.2 kcal/mole, to a lower temperature regime, where the activation energy is equal to 21.9 kcal/mole.

Stephens/Greville/Bennis 31 34

appeared to be a regime with a lower activation energy for oxidation. By grouping all of the 750-1100°C data together, the following correlation for k^2 was obtained:

$$k^2 \text{ (gm}^2\text{/cm}^4\text{-hr)} = 1.843 \times 10^4 \exp(-52,232 \text{ (cal/mole)}/RT) \quad (12)$$

Similarly, by including the data from Pask at 600°C, and the data from Abendroth at 700°C, along with the values of k^2 obtained from the fits given in the first three entries of Table 11, we obtained the following correlation for k^2 over the temperature range 550-700°C:

$$k^2 \text{ (gm}^2\text{/cm}^4\text{-hr)} = 1.062 \times 10^{-2} \exp(-21,894 \text{ (cal/mole)}/RT) \quad (13)$$

The two correlation are plotted in Figure 17, and crossover at approximately $1/T=0.00941$, ie., at 790°C.

Although we don't have detailed x-ray diffraction data to account for this transition in oxidation kinetics, the results of previous studies (11, 12) do suggest that the transition from the high temperature regime to low temperature oxidation kinetics could be caused by the change in the dominant oxide species. That is, the high temperature data obtained were obtained at relatively short times where the spinel $(\text{Fe,Co,Ni})_3\text{O}_4$ is the dominant oxide species, while the lower temperature data - especially the results obtained in the present study - are obtained in a temperature range where the Fe_2O_3 type oxide constitutes a significant fraction of the oxide scale. Further work is suggested to fully document this transition in oxidation kinetics.

Summary and Conclusions

1. The "once-through" processing study for Cu-brazed Fe-29Ni-17Co alloy leads has shown that considerable grain growth can occur as a result of time spent at 1100°C. A typical grain size which would be expected following such processing is ASTM #4-5.
2. An isothermal grain growth study has shown that the mean intercept length of Fe-29Ni-17Co alloy can be described as a function of time and temperature using a power law equation. For the wire material studied, we observed generally larger values of intercept length at 1100°C for material which started processing in the cold-worked, as opposed to mill-annealed, condition. In general, the total time of thermal exposure of Fe-29Ni-17Co leads at $\geq 900^\circ\text{C}$ needs to be controlled to avoid excessive grain growth.
3. Oxidation in air at temperatures between 550° and 700°C has indicated that the Fe-29Ni-17Co alloy oxidizes according to a parabolic kinetic law. This observation is consistent with the results of previous investigators (5, 11, 12) who studied oxidation of this alloy, for the most part, at significantly higher temperatures. Analysis of the temperature dependence of oxidation in Fe-29Ni-17Co alloy indicates that parabolic oxidation at higher temperatures proceeds with an activation energy of 52.2 kcal/mole, while at lower temperatures it occurs at a somewhat lower activation energy, 21.9 kcal/mole. The transition in oxidation occurs around 750-790°C, and could be related to the transition in oxide scale from completely spinel type $(\text{Fe,Ni,Co})_3\text{O}_4$ at higher temperatures to increasing amounts of Fe_2O_3 at lower temperatures.

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Stephens/Greulich/Beavis

32

34

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References

1. R. L. Bertolotti, "Thermal Expansions of Kovar and Ceramvar and Seals of These Materials to Alumina," Report SAND74-8003, Sandia Laboratories, Livermore, CA, September, 1974.
2. "Standard Specification for Iron-Nickel-Cobalt Alloys for Metal-to-Ceramic Sealing Applications," ASTM F-1466, to be published in December, 1993 in 1993 Annual Book of ASTM Standards, Volume 10.04. Philadelphia, PA: American Society for Testing and Materials; "Standard Specification for Iron-Nickel-Cobalt Alloy," ASTM F-15, 1992 Annual Book of ASTM Standards, Volume 10.04.
3. C. S. Pande and S. P. Marsh, "The Analytical Modeling of Normal Grain Growth," JOM, 44, 25-29 (September, 1992).
4. R. T. DeHoff, "The Estimation of Particle-Size Distributions from Simple Counting Measurements Made on Random Plane Sections," Trans. A.I.M.E., 233, 25-29 (January, 1965).
5. J. A. Pask, "New Techniques in Glass-to-Metal Sealing," Proceedings of the I.R.E. - Waves and Electrons Section, 36, 286-289 (February, 1948).
6. E. E. Underwood, Quantitative Stereology. Reading, MA: Addison-Wesley, 1970.
7. P. A. Beck, "Annealing of Cold Worked Metals," Advances in Physics: A Quarterly Supplement of the Philosophical Magazine, 3 (#11), 271-322 (July, 1954).
8. E. A. Holm and D. J. Srolovitz, "Particle Shape Effects in Inhibited Grain Growth," Acta Metallurgica, in press.
9. J. E. Burke, "Some Factors Affecting the Rate of Grain Growth in Metals," Trans. A.I.M.E., 180, 73-91 (1949).
10. P. Cotterill and P. R. Mould, Recrystallization and Grain Growth in Metals, New York: John Wiley and Sons, 1976, pp. 289-291.
11. R. A. Piscitelli, S. K. Rhee and F. N. Bradley, "Oxidation of Fe-29Ni-17Co Alloy," Journal of the Electrochemical Society: Solid State Science and Technology, 123, #6, 929-933 (June, 1976)
12. R. P. Abendroth, "Oxide Formation and Adherence on an Iron-Cobalt-Nickel Glass Sealing Alloy," Materials Research and Standards, 5, 459-466 (September, 1965).
13. J. J. Stephens, unpublished research. Sandia National Laboratories, Albuquerque, New Mexico. October, 1991.

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14. B. D. Barstow, D. P. Whittle and G. C. Wood, "Diffusion-Controlled Growth of Solid Solution Scales on Nickel-Cobalt Alloys," Corrosion Science, 16, 57-69 (1976).
15. T. B. Massalski, editor. Binary Alloy Phase Diagrams, Metals Park, Ohio: American Society for Metals, 1986. vol. 1, p. 1087.
16. W. H. Kohl, Handbook of Materials and Techniques for Vacuum Devices, New York: Reinhold Publishing Corp., 1967. pp. 425-429.
17. M. R. Notis, "Decarburization of an Iron-Nickel-Cobalt Glass Sealing Alloy," Journal of the American Ceramic Society, 45 (#9), 412-416 (September, 1962).

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