U.S. Department of Energy

Final Technical Report

Project: DE-FC07-06ID14753 University of Missouri-Rolla

Title: Ni-Si Alloys for the S-I Reactor-Hydrogen Production Process Interface

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Goals/Summary

The overall goal of this project was to develop Ni-Si alloys for use in vessels to contain hot, pressurized sulfuric acid. The application was to be in the decomposition loop of the thermochemical cycle for production of hydrogen. In order to perform this function the alloy needed to meet the corrosion standard of less than 5 mpy and be able to be fabricated into pipes. The specific goals are below.

- 1) Determine mechanism for protective nature of alloy
 - a) Passivation reaction
 - b) Stability of protective film under corrosion-erosion
 - c) Cause of Ti degradation and possible solution
- 2) Evaluate performance under service conditions and improve where possible
 - a) Testing in hot, pressurized sulfuric
 - b) Erosion testing in closed loop
- 3) Develop wrought analog to cast alloy, including characterization of high temperature properties
 - a) Alloys cold rolled and annealed
 - b) Hot deformation evaluated
 - c) Mechanical properties measured
- 4) Fabricate vessels for testing

The erosion testing required the construction of an apparatus at INL. This apparatus was never built as the program funds were reduced. Therefore goals 1b, 2b, and 4 were never attempted. All other goals were completely accomplished.

Materials

All alloys which were investigated were based on the intermetallic compound Ni_3Si .

The intermetallic has the $L1_2$ crystal structure and is inherently ductile. Limitations in the room temperature ductility were mitigated by adding either Ti or Nb. Previous work by the Principal Investigator had shown the Ti additions were detrimental to the corrosion performance in 70% boiling sulfuric acid. Therefore most of the study concentrated on Nb containing alloys. However, some Ti containing alloys were included in an effort to determine the cause of the lowered corrosion resistance. Additionally a rare earth containing alloy was studied to determine if the rare earth would be incorporated into the passive film formed on the alloy during corrosion. The list of alloys studied is given in the table below. Nickel silicon alloys were prepared by induction melting of the metal components in a graphite mold under an Argon atmosphere.

Code	Alloy (at%)	Comments
NiSi ₂₂	NiSi ₂₂ B _{0.5}	No Nb
2BM1	NiSi ₂₀ Nb ₂ B _{0.5}	Lower Nb than baseline
2B2	NiSi ₁₈ Nb ₅ B _{0.5}	Higher Nb, lower Si
2B-B	NiSi ₂₀ Nb ₃ B _{0.5}	Baseline heat
A	NiSi ₂₀ Nb ₃ B _{0.5}	Another baseline heat
2B0-M1	NiSi _{21.4} Nb _{1.6} B _{0.5}	Commercial new composition (missed composition)
2B0-M1B	NiSi _{21.4} Nb _{1.6} B _{0.5}	Commercial new redo
MM1C	NiSi ₂₀ Nb ₃ B _{0.5} +0.5%Ce	Rare earth modification
E (Ni-Si-Ti)	NiSi ₂₀ Ti ₃ B _{0.025}	Ti in place of Nb
J	NiSi ₂₀ Nb ₃ Ti ₁ B _{0.05}	Ti modified
2B-10Fe	NiSi ₂₁ Fe _{7.5} Cu ₉ Nb ₂ B _{0.5}	Lower cost iron heat

Composition variations were studied in the Nb containing alloys. Different ratios of Si/Nb were studied. Increased Si amounts led to higher hardnesses and lower ductility and were therefore not pursued further. The presence of G phase (a ternary intermetallic of Ni-Si-Nb) was looked at in terms of any detrimental effects on the alloy. Eliminating G-phase was a matter of reducing Nb contents until the solubility limit was reached. The figure shows the amount of G-phase in the microstructure versus the Nb addition of the alloy. Solubility seems to around 1.6%

Figure. G-phase amount versus alloy Nb concentration.

A commercial heat was purchased from Haynes International with the Nb content reduced to the apparent solubility limit. Despite the low level of Nb, some G-phase was still apparent in the microstructure, although it was considerably less. The figure below shows a typical microstructure of an as-cast alloy. The phase compositions as determined by EDS are given in the table.

Element	Point 1 $\text{Nb}_6\text{Ni}_{16}\text{Si}_7$		Point 2		Point 3 $\text{Ni}_3\text{Si} + \text{Nb?}$		Point 4 $\text{Ni}_{31}\text{Si}_{12} + \text{Nb}$ or $\text{Ni}_2\text{Si} + \text{Nb}$		Point 5 $\text{Nb}_6\text{Ni}_{16}\text{Si}_7$		Point 6	
	Wt%	At%										
Si	11.2	23.4	05.5	11.3	10.3	19.8	16.4	29.2	11.8	24.2	07.7	15.2
Nb	33.5	21.2	11.1	06.9	06.4	03.7	01.9	01.0	30.3	18.8	05.9	03.5
Ni	55.3	55.4	83.3	81.8	83.3	76.5	81.7	69.7	57.9	57.0	86.4	81.3

Figure. As-cast typical microstructures showing various phases and compositions.

The performance of the alloys was considerably better after homogenization, and most of the tests and evaluation were carried out on samples which were homogenized. The most common homogenization treatment consisted of heating the samples to 950C for 4 days in an Argon atmosphere. A typical microstructure after homogenization is shown below in the figure. As can be seen the number of phases has been reduced to two.

The phase compositions as determined by EDS are given in the table.

Element	Point 1		Point 2	
	Wt%	At%	Wt%	At%
Si	16.36	29.18	09.53	18.44
Nb	01.79	00.97	06.38	03.73
Ni	81.85	69.85	84.09	77.83

Figure. Homogenized microstructure and compositions

Prior work by the PI had shown that the addition of iron in amounts greater than a few percent resulted in the formation of Fe_3Si , which is very brittle. While the material is expected to have excellent corrosion resistance, the mechanical properties would be unsuitable. Alloying theory states that the e/a (valence electron to atom) ratio should control stability of the phase. Extending the crystal structure of Ni_3Si into regions of higher iron amounts needs a balancing alloying element to help to maintain the e/a ratio and continue to produce the ductile L12 crystal structure. The electronic structure of copper is such that the addition of 1.2 Cu atoms to each Fe atom as a replacement for Ni should maintain the alloying ration and hence the structure. Hence a heat was purchased from Haynes Corporation to specifications written by Missouri S&T.

The nominal and actual composition of the heat, called 2B-10Fe are shown in the table. Haynes missed the composition due to an incorrect silicon fading assumption and hence the heat is too high in Si. This contributed to the material being very brittle and it exhibited significant cracking before even being sectioned into smaller samples.

Table. Composition of the iron containing heat 2B-10Fe.

	Aim(wt%)	Actual(wt%)	Actual(at%)
Ni	74.9	65.9	58.3
Si	7.0	12.4	23.0
Fe	8.0	7.9	7.3
Cu	7.7	11.1	8.9
Nb	2.4	3.5	2.0

The microstruture which resulted is shown in the figure below. There was a signifcaint amount of the desired beta phase (~50%), but also a eutectic microconstituent which contained a significant amount of the Fe, probably in a Fe₃Al phase mixed with beta (~30%) and G-phase.

Figure. Microstructure of iron containing heat 2B-10Fe and compositions.

	Composition by EDS(wt%)			Area ratio			Composition(wt%)	
	eutectic	Beta	G	eutectic	Beta	G	cal.	Actual
Si	3.8	8.7	7.7	0.32	0.52	0.16	7.0	12.4
Fe	16.9	3.6	4.3	0.32	0.52	0.16	8.0	7.9
Ni	66.5	81.7	69.8	0.32	0.52	0.16	74.9	65.9
Cu	12.9	5.8	3.4	0.32	0.52	0.16	7.7	11.1
Nb			14.7	0.32	0.52	0.16	2.4	3.5

The elemental analysis of the various regions and their area ratios are shown in the table. There was some solubility of the Fe and Cu in the beta phase which is desirable, however the extensive solubility hoped for was not found. Additionally, there was significant oxygen (not shown in table) on the surfaces indicating that the Fe increased the rate of oxide formation. This may indicate a faster passivation response.

It was concluded that attempting to guess compositions and casting them by a trial and error basis was not very productive. A thermodynamic modeling approach is recommended and NETL-Albany has agreed to do some modeling with the extensive nickel databases they possess, but at the conclusion of this study, no work had been carried out.

Corrosion testing

Standard pressure testing was carried out in solutions of sulfuric acid at the boiling point. The most commonly used strength was 70%, because previous work had shown that it was one of the most aggressive solutions. While higher levels of sulfuric acid may at first seem to be the tougher test, the levels close to the cross-over from oxidizing to reducing behavior (~65% in sulfuric acid) actually are the worst. Therefore, the assumption is that good corrosion rates in 70% boiling sulfuric are good for all higher solutions. Some testing was done in boiling 80% to test this and also to study the effect of passivation in this solution.

The alloys were cut into 1cm x 1cm x 4mm dimensions and then polished. The samples were measured and weighed prior to immersion in the corrosive solution. Samples were removed at various times, washed, dried and weighed before being immersed again. The solution was checked periodically to ensure that the solution strength did not change due to evaporation.

The figure below shows typical results from the testing. The weight lost is normalized to the area of the sample based on the initial measurement. After an initial rapid weight loss the rate slowed considerably. NACE testing standards call for testing for 3 days (4320 minutes) and 6 days (8640 minutes) to look at the passivation behavior

of an alloy. In the case shown below passivation appears to have occurred during the first 100 to 400 minutes depending on the alloys condition.

Fig. Corrosion testing example (2B0M1-B) for homogenized (unroll) and two cold rolled samples.

Analyses of these results were performed by transforming the data by taking the natural logarithm of time and weight loss. The transformed data is shown below. The data falls into a number of linear regimes whose slope is indicative of the corrosion mechanism occurring. The early stages of corrosion show a linear behavior (slope of ~ 1) followed by a passivated region of very slow corrosion. The slope in the passivate region is used to calculate the corrosion rate in mpy (mils per year). The start of the passivated region determines the time to passivation.

Fig. Kinetic analysis of rolled data above. Two different corrosion regimes are shown. The first is a linear growth region and the second is the passivated region.

Results for all alloys tested are shown in the following table. All alloys which did not contain titanium and which had silicon amounts greater than 19% showed excellent performance. Passivation times varied considerably and more attention needs to be paid to how to reduce the time for passivation as some of the times are rather long. Rolling appeared to have a positive effect on shortening passivation time.

Table. Corrosion testing data

Alloy		Si content (at%)	Slope on passivation	mpy at passivation	Time for passivation (mins)
NiSi ₂₂	As cast	22	0.035	6.8	150
2BM1	HT	20.8	0.005	0.9	320
2BM1(10% setting)	10 pass	20.8	0.005	1.2	300
2B0-M1B	HT	20.4	0.02	4	450
2B0-M1B(10% setting)	10 pass	20.4	0.05	6.1	90
2B0-M1B(20% setting)	10 pass	20.4	0.02	2	80
Alloy E (Ni-Si-Ti)	As cast	19.8	0.056	39	900
2B-B	HT	19.7	0.004	2.6	1500
Alloy A (Ni-Si-Nb)	As cast	19.7	0.582?	8.2	480
MM1C	HT	19.7	0	0	320
MM1C	As cast	19.7	0.08	13.7	110
2B2(7% setting)	10 pass	18	0.07	22.4	700
2B2	HT	18	0.14	64.5	370
Alloy J	As cast	16.2	0.03	9	540

Several samples were tested for the lasting effect of passivation. Samples were corroded well into the passivation region and then stopped. The samples were then removed, washed and dried before being placed on a shelf for several weeks. The testing was restarted with these samples and the corrosion rates matched up exactly with those measured previously. The results of two such tests are shown in the figure below.

Samples were also tested in 80% boiling sulfuric acid. The test resulted in significantly shorter passivation times and lower overall corrosion rates than the same material tested at 70%. Samples were also corroded at 80% and then immersed in 70%. This was to show the ability to prepassivate the alloy before use. The idea is to treat pipes by running higher concentrations of acid through first to pretreat them. The subsequent corrosion rate would be lower and the total ion content dissolved in the new solution would be low. This proved to be effective in lowering the corrosion rate in 70%. The results of these tests is shown in the figure.

Figure. Results of tests of 2B0M1-B in 70%, 80%, and 80% followed by 70% boiling

sulfuric acid. Lower rates in 80% were maintained in 70% after pre-exposure to 80%.

A comparison of the mpy of samples of 2B0M1-B as a function of time for 70 and 80% solutions are shown in the figure. As suggested above, the samples performed extremely well in both solutions. The rates become identical after passivation has occurred, with the

samples tested in 80% boiling sulfuric acid just passivating in a shorter period of time.

Fig. Comparison of mpy for 70 and 80% boiling sulfuric acid. After passivation, both have identical performance.

Tests were undertaken at INL by Dr. Thomas Lilo using the pressurized test autoclave. The tests were carried out at both 70 and 96% sulfuric acid. Most samples performed better than any other alloy tested and easily met the 5 mpy target. Results were very similar to the standard air pressure tests and most alloys ranked the same for both tests.

Compared to standard pressure tests, the tests conducted at high temperatures and pressures appeared to passivate faster. A comparison of results in 70% Sulfuric is shown in the figure. The same alloys were tested at 1 atmosphere at the boiling point and at 300C at 37.4 atm. Higher temperature appears to lower the corrosion rate. Possible reasons to be evaluated include effect of pressure on SiO₂ stability and faster passivation due to higher temperature. We are looking into information on stability of different quartz phases with pressure. This seems unlikely, but still possible.

Fig. Comparison of tests carried out at 1 and 37.4 atmospheres .

Looking at the data, it is possible to imagine that the higher temperature curves could be slid to the right and tacked onto the end of the lower temperature curves. This idea seems too simple and is probably wrong, but would make sense if the temperature and pressure change had a minimal effect on the corrosion rate, but only sped up the film formation.

Corrosion mechanism

In order to further the design of the alloys, an understanding of the corrosion mechanism is critical. Therefore significant effort was invested in attempting to understand the mechanism involved in the behavior of the alloys. Once this mechanism is understood, additional alloying routes may then be obvious to undertake to further improve the performance.

Sample	Ni	Si	O	Nb	S
Baseline	70.57	14.25	9.91	5.27	-
A 1 Min	1.26	24.41	68.89	1.72	3.72

A 30 Min	0.73	32.19	65.17	0.22	1.69
A 3 day	2.44	25.90	65.39	0.47	5.80
A 6 day	1.03	31.31	64.39	0.10	3.16

Peak	Ni	Si	O	Ti	S
Baseline	69.17	16.22	11.73	2.88	-
E 1 Min	1.91	25.71	68.05	-	4.32
E 30 Min	2.05	24.53	67.01	-	6.41
E 3 day	-	35.30	63.72	-	0.98
E 6 day	-	34.21	64.11	-	1.68

Corroded surfaces were studied using Auger and XPS in order to determine the nature of the film produced during passivation. The tables above show the composition of the film at different stages during passivation for a baseline composition (A) and a Ti containing alloy (E). The film in each case shows considerable Si and O amounts in a ratio that could be SiO_2 . For the baseline alloy, there is also a small concentration of Nb and a significant level of Ni and S. The Ti containing alloy has less sulfur and no Ni. It is suspected that the extra Ni in alloy A is from NiSO_4 .

AES results show that the Si, that is present during different stages also changes its chemical bonding. The figure below shows the evolution of the Si peak as the surface goes from unexposed to passivated. Originally the Si exhibits highly metallic character as would be expected from Si that is part of the Ni_3Si phase. After exposure the character changes and becomes fairly unspecific, as would be expected for SiO_2 and particularly the amorphous form. This is not definitive proof that the film is amorphous but suggests it. Proving the film is amorphous and not some form of crystalline SiO_2 is difficult.

Fig. AES spectra for alloy A. a) untreated. b) air at 900C c) nitric acid.

Fig. Surface of corroded baseline samples versus exposure time.

The figure above shows the surface of a sample that was corroded in 70% boiling sulfuric acid. The surface has a rough appearance and shows what appears to be some porosity. Analysis of the debris found at the bottom of the corrosion apparatus indicates that material is lost from the surface. The weight of the debris versus time is shown in the figure. As the debris is produced mostly during the linear portion of the corrosion process it suggests that the oxide spalls off during this portion, but then stops spalling and forms an impermeable film.

Fig. Weight loss and debris formation versus time during corrosion.

The debris analysis was filtered, washed, dried and analyzed in the SEM. There are Si, O and about 2-3 at% Nb signals in EDS, but no Ni or S signals. A micrograph of a debris particle, shown below, shows the appearance of brittle fracture surfaces.

Fig. Micrograph of debris formed during corrosion, mostly SiO_2 .

Measurements of the film thickness show a behavior consistent with that discussed above. The film forms quickly and then the thickness fluctuates around 20 microns. Apparently spalling keeps reducing the thickness until passivation occurs.

2B0M1B		
exposure time	oxide thickness	
3 min		18.8 ± 7.4
50 min		37.5 ± 5.1
4 hr		11.9 ± 3.7
13 hr		3.4 ± 1.3
63 hr		16.8 ± 6.7

Cross sections of corroded samples were used to measure the thickness of the film and also the effect of corrosion on any internal structures. The film is shown in the figure below to have a scalloped appearance to the thickness. Thickness measurements are the averages of the local thickness. Apparently the corrosion does not proceed as a linear front, but is affected by the local microstructure. The sample shown is an example of incomplete homogenization and shows that there is internal oxidation occurring at certain microstructural features. Since the alloy passivated eventually, the film must cut off the oxidation diffusion and stop the internal oxidation. Fully homogenized samples did not have any internal oxidation.

Fig. Cross-section of a corroded sample which shows incomplete homogenization. Internal oxidation is observed, although the alloy eventually passivated.

A theory for the mechanism of corrosion and eventual passivation of Ni-Si alloys is presented as follows. The sulfuric acid attacks the Ni_3Si phase by forming SiO_2 and NiSO_4 . The NiSO_4 is soluble in sulfuric acid and leaches out, creating a fragile porous structure of SiO_2 . Spalling of this structure leads to a linear kinetics region early in the corrosion process. The amount of SiO_2 versus NiSO_4 is controlled by the Si content and as Ni is lost from the surface, the Si content rises at the interface. An increased level of Si eventually stops leading to NiSO_4 formation and the film passivates.

Simulations of the process using Factsage software indicates that NiSO_4 is stable under these conditions and will remain so until the alloy concentration reaches 33 atomic percent. If this is the mechanism which governs the corrosion process, there should be a detectable amount of Si enrichment found at the metal-oxide interface.

Fig. FIB-SEM results from sputtering down into the corroded film. An EDS analysis of the sputtered cross-section shows the Si signal increasing below the metal-oxide interface.

A FIB-SEM analysis of a corroded sample shows a significant increase in the Si signal below the metal-oxide interface, but no corresponding O increase at that point. There is also an apparent increase in the Nb and S signal at the interface. This result was not repeatable in all of the samples, so should not be considered definitive. However, there is support for the theory presented above.

Air oxidation studies

Given the use of this material in pipes containing hot, pressurized sulfuric acid it was felt important to study the high temperature air oxidation behavior of this material as the

outside of the pipe would be hot. Samples were placed in furnaces at either 700 or 900C and the weight change measured versus time. The new alloy composition, the rare earth containing material and the Ti containing material were all tested.

	Oxide thickness(um)		Normalized weight gain (mg/cm ²)	
	700°C (1008 hrs)	900°C (672 hrs)	700°C (1008 hrs)	900°C (672 hrs)
MM1C	10.6 ± 3.0	33.7 ± 8.1	6.4 ± 0.1	3.4 ± 0.2
2B0M1B	11.1 ± 2.9	37.3 ± 10.4	1.2 ± 0.2	2.5 ± 0.3
Alloy E	13.9 ± 1.3	1.8 ± 0.3	0.5 ± 0.1	3.7 ± 0.4

A weight gain was observed in all cases with parabolic behavior being exhibited as shown in the figure below. The oxide thickness at set times and weight gains are compared in the table. All of the alloys produced modest weight gains except the rare earth alloy (MM1C) at 700C. This exhibited anomalously high weight gains, possibly indicating a pesting problem at intermediate temperatures.

Fig. Air oxidation results on three alloys. Note anomalous behavior of MM1C at 700C.

Activation energies and k values for these alloys are shown in the table below. No value could be determined for MM1C due to the behavior of that alloy.

Cold and warm rolling experiments

The ability to fabricate by cold rolling shapes from this material was evaluated. In addition, the ability to improve homogenization and shorten the homogenizing procedure

was investigated. The following materials were used in the rolling experiments:

- ❖ 2BM1, $\text{NiSi}_{20}\text{Nb}_2\text{B}_{0.5}$
- ❖ 2B2, $\text{NiSi}_{18}\text{Nb}_5\text{B}_{0.5}$
- ❖ 2BM2, $\text{NiSi}_{20.4}\text{Nb}_3\text{B}_{0.5}$
- ❖ 2B0M1B, $\text{NiSi}_{21}\text{Nb}_{1.6}\text{B}_{0.5}$

The room temperature mechanical properties of the alloys are shown in the table.

Homogenization is important to reduce hardness and increase ductility. Percent elongation was typically in the range of 2 to 4% for all alloys.

Alloy	Hardness(RC)			UTS (Mpa)	Elongation (%)
	As cast	900°C 1 Day	950°C 4 Day		
$\text{NiSi}_{18}\text{Nb}_5\text{B}_{0.5}$	-	45.0± 1.4	39.7± 2.4	-	0.7 ³
$\text{NiSi}_{20}\text{Nb}_2\text{B}_{0.5}$	46.4± 2.7	43.3± 1.5	42.5± 1.5	-	-
$\text{NiSi}_{20}\text{Nb}_3\text{B}_{0.5}$	-	44.4± 1.9	41.2± 1.2	876± 17 ²	3.6± 1.6 ²
$\text{NiSi}_{21}\text{Nb}_{1.6}\text{B}_{0.5}$	-	-	39.6± 1.3	810± 33 ²	1.9± 0.6 ²

Heat treatment: ²950°C 4 Day; ³900°C 1 Day

Rectangular samples were cut to about 30x10x3 mm from the starting materials and then rolled using the small rolling mill at Missouri S&T. The rolling procedure consisted of:

1. Heat samples to rolling temperature
2. Set reduction & Roll
3. Anneal (950C, 5 hr.)
4. Furnace or air cooling to rolling temperature
5. Record hardness and reduced dimensions

The rolling temperature was typically 300°C or room temperature. Prior to rolling samples were homogenized at 950°C 4 days. Samples were also surface ground with #400 SiC paper to remove any surface oxide. The amount of reduction set on the mill should have controlled the amount of reduction, but the samples were too hard for the capacity of the mill and no reduction greater than about 12% was achieved.

Reduction of $\text{NiSi}_{21}\text{Nb}_{1.6}\text{B}_{0.5}$ with each rolling pass at 300°C for different reduction settings is shown in the figure below. The original thickness was 3.05mm. The total reduction was 44% for the 10% reduction setting(10 pass) and 61% for the 20% reduction setting(10 pass).

Fig. Individual reductions per pass for 2B0M1B, NiSi₂₁Nb_{1.6}B_{0.5}

The hardness increased upon rolling and after each pass, was lowered by an annealing operation as described above. The figure shows a typical hardness change with each pass and each anneal for NiSi₂₀Nb₂B_{0.5}. The hardness did not change significantly with rolling amount. There was no softening associated with increased homogeneity. Although the reduction per pass was limited to 12%, this was a limitation of the rolling mill and not the material. It has not yet been determined what the maximum reduction per pass is.

Fig. Hardness of NiSi₂₀Nb₂B_{0.5} for each rolling pass and annealing step at 300°C (total reduction was 61% for 20% reduction setting (10 pass))

The microstructure of the alloys was simplified by homogenization, however, the

segregation which occurred in the casting was not eliminated. The figure below shows the as-cast microstructure versus the homogenized for 4 day condition. It can clearly be seen that there are composition variations still present even after 4 days.

The microstructures after rolling and annealing are also shown in the figure below for comparison. The microstructure appears to be completely homogenized. This is probably the reason for the improved corrosion performance of the rolled materials when compared to the non-rolled material.

Fig. Microstructure of NiSi₂₀Nb₂B_{0.5} in different conditions. (a) as cast (b) heat treated 950°C 4 days (c) after 6 rolling passes (furnace cooling). (d) after 12 rolling passes (furnace cooling)

Another effect of the rolling would be the potential reduction of the G-phase in the structure. The average size of the G-phase, the total amount and number of particles per

unit area were measured before and after rolling.

	NiSi ₁₈ Nb ₅ B _{0.5}		NiSi ₂₀ Nb ₂ B _{0.5}		NiSi ₂₁ Nb _{1.6} B _{0.5}	
	HT	Rolled	HT	Rolled	HT	Rolled
size (um)	8.3±4.4	5.3±3.7	4.3±3.6	4.2±3.4	5.5±3.8	2.3±2
counts/mm ²	2500	6100	4700	5200	1330	4700
area fraction	16	14	5.4	4.4	1.4	1.9

There was little effect of rolling on the total amount of G-phase indicating that this was close to the equilibrium amount. However, there was a significant size reduction and redistribution of the G-phase which could also have beneficial effects on the properties.

Rolling of the Ti containing alloy E was unsuccessful. The materials broke into pieces early in the rolling process. An examination of the microstructure shows microcrack between the grains millimeter deep within the material. It is possible a brittle intergranular phase was formed which is too small to detect in the SEM.

Fig. Alloy E after cold rolling.

The temperature of rolling was investigated after learning (next section) that the ductility was higher at room temperature than at 300C. The figure below shows the results of a comparison of RT versus 300C. There was little difference and the maximum amount of reduction allowed by the capacity of the rolling mill was not effected.

Fig. Reduction of $\text{NiSi}_{18}\text{Nb}_5\text{B}_{0.5}$ with rolling pass at room temperature and 300°C

High temperature properties

Compression tests were carried out at various temperatures at INL for three alloys. Cylindrical samples were fabricated using electrodischarge machining. The tests were performed in an argon atmosphere and used a strain rate of $3 \times 10^{-4} \text{ s}^{-1}$ and used temperatures ranging from RT up to 950C.

The yield strength results for the three alloys are shown in the figure below. Nb added considerable high temperature strength to the alloys and all materials have excellent strength values. A maximum occurred in the yield strength of the Nb containing alloys at about 500C. Considerable strength was retained at temperature up to 900C.

One question of interest is the ability of these alloys to be hot rolled for fabrication into pipe. Based on the yield strength values it seems that temperatures above 800C would be the most likely for good hot workability.

Fig. Yield stress of the $\text{Ni}_3(\text{Si,Nb})$ alloys as a function of test temperature. Compression tests were carried out in Argon atmosphere at a strain rate of $3 \times 10^{-4} \text{ s}^{-1}$

The figure below shows the actual stress-strain curves of $\text{NiSi}_{18}\text{Nb}_5\text{B}_{0.5}$ at three different temperatures. At 200°C , it seems to indicate a ductility minimum. The results for $\text{NiSi}_{20}\text{Nb}_2\text{B}_{0.5}$ were similar. Despite this minimum, the rolling tests were still excellent at 300°C .

Fig. Stress-strain curves of $\text{NiSi}_{18}\text{Nb}_5\text{B}_{0.5}$ at different temperatures. At 200°C , it seems to indicate a ductility minimum.

Summary

A three year investigation into the development of Ni-Si alloys for use in the thermochemical process for hydrogen generation shows that the alloy system shows excellent potential for use in this application, as well as a number of other applications where sulfuric acid is being used. It also has potential for employment in a number of other atmosphere, such as supercritical CO₂. Mechanical properties are excellent for the temperature ranges anticipated and fabrication has been demonstrated. No actual service testing was performed, however. A corrosion mechanism has been proposed which could lead to further improvements and modifications of the materials. Further work would be necessary in order to commercialize this alloy for industrial use.

Future work

It is recommended that further development work be undertaken to answer the remaining questions about the use of this system of alloys for energy related activities. These studies should include fabrication by hot rolling; long time exposure to high temperatures; study of the potential pitting issue in air oxidation, and improving the passivation times. Also of interest would be the applicability to other environments such as sulfidation and supercritical CO₂.