

Final Report – Computer Aided Design of Advanced Turbine Airfoil Alloys for Industrial Gas Turbines in Coal Fired Environments

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ABSTRACT

Recent initiatives for fuel flexibility, increased efficiency and decreased emissions in power generating industrial gas turbines (IGT's), have highlighted the need for the development of techniques to produce large single crystal or columnar grained, directionally solidified Ni-base superalloy turbine blades and vanes. In order to address the technical difficulties of producing large single crystal components, a program has been initiated to, using computational materials science, better understand how alloy composition in potential IGT alloys and solidification conditions during processing, effect castability, defect formation and environmental resistance. This program will help to identify potential routes for the development of high strength, corrosion resistant airfoil/vane alloys, which would be a benefit to all IGT's, including small IGT's and even aerospace gas turbines. During the first year, collaboration with Siemens Power Corporation (SPC), Rolls-Royce, Howmet and Solar Turbines has identified and evaluated about 50 alloy compositions that are of interest for this potential application. In addition, alloy modifications to an existing alloy (CMSX-4) were also evaluated. Collaborating with SPC and using computational software at SPC to evaluate about 50 alloy compositions identified 5 candidate alloys for experimental evaluation. The results obtained from the experimentally determined phase transformation temperatures did not compare well to the calculated values in many cases. The effects of small additions of boundary strengtheners (i.e., C, B and N) to CMSX-4 were also examined. The calculated phase transformation temperatures were somewhat closer to the experimentally determined values than for the 5 candidate alloys, discussed above. The calculated partitioning coefficients were similar for all of the CMSX-4 alloys, similar to the experimentally determined segregation behavior. In general, it appears that computational materials science has become a useful tool to help reduce the number of iterations necessary to perform laboratory experiments or alloy development. However, we clearly are not able to rely solely on computational techniques in the development of high temperature materials for IGT applications. A significant amount of experimentation will continue to be required.

EXECUTIVE SUMMARY

Currently, alloys such as IN738 and IN792 (and their derivatives) are the baseline alloys used for many industrial gas turbine (IGT) applications. These alloys are polycrystalline materials that exhibit good hot corrosion resistance but do not meet the increasing temperature demands of the power industry. To increase material temperature capabilities for IGT's, the use of single crystal (SC) or directionally solidified (DS) turbine blades will be required. Processing problems, such as castability, that come from fabricating inherently large IGT components must be factored into the selection of an appropriate SC/DS IGT alloy. Some of the single crystal alloys presently considered for IGT applications include CMSX-4 and PWA 1483.

PWA 1483 demonstrates an acceptable level of hot corrosion resistance and castability for IGT applications but exhibits limited strength in comparison to other single crystal alloys (i.e. CMSX-4). CMSX-4, developed for aerospace applications, is a second-generation, single crystal alloy that exhibits high strength at elevated temperatures but demonstrates poor hot corrosion resistance and castability. Other alloys are also being considered but have problems with hot corrosion resistance, castability or strength.

The successful use of single-crystal and directionally solidified alloys in IGT applications is contingent upon overcoming processing problems such as defect formation, and maintaining microstructural stability once in service. The increased number of elemental additions in a Ni-based superalloy and the complex interactions of these additions reveal a need to investigate elemental variation effects on microstructural stability, phase transformation temperatures, and material segregation behavior.

Recent initiatives for fuel flexibility, increased efficiency and decreased emissions in power generating industrial gas turbines (IGT's), have highlighted the need for the development of techniques to produce large single crystal Ni-base superalloy turbine blades and vanes. In order to address the technical difficulties of producing large single crystal components, a program has been initiated to, using computational materials science, better understand how alloy composition in potential IGT alloys and solidification conditions during processing, affect castability, defect formation and environmental resistance. This program will help to identify potential routes for the development of high strength, corrosion resistant airfoil/vane alloys, which would be a benefit to all IGT's, including small IGT's and even aerospace gas turbines. During the first year, collaboration with Siemens Power Corporation (SPC), Rolls-Royce, Howmet and Solar Turbines has identified and evaluated about 50 alloy compositions that are of interest for this potential application. Several visits to SPC have been taken by the student working on this project to utilize computational software at SPC to evaluate the 50 alloy compositions. From these preliminary results, 5 alloys were experimentally evaluated using small arc-melted buttons. The results obtained from the experimentally determined phase transformation temperatures did not compare well to the calculated values in many cases. Based on the limited agreement between the experimentally determined and calculated values, none of the alloy compositions were selected for further work. Instead, further evaluation of one of the alloys being considered for IGT

applications, CMSX-4 alloys with small additions of boundary strengtheners (i.e., C, B and N), was considered more appropriate. Therefore, the ability to use computational techniques to evaluate the CMSX-4-based alloys would be very beneficial for future potential IGT applications. The calculated partitioning coefficients were similar for all of the CMSX-4 alloys, similar to the experimentally determined segregation behavior. In general, it appears that computational materials science has become a useful tool to help reduce the number of iterations necessary to perform laboratory experiments or alloy development. However, we clearly are not able to rely solely on computational techniques in the development of high temperature materials for IGT applications. A significant amount of experimentation will continue to be required. This program is also a unique opportunity to train graduate and undergraduate students in the field of high temperature materials and to stimulate industrial/university interaction.

REPORT DETAILS

Year 1:

The effort during the first year utilized a design approach aimed toward the development of a set of alloys for fuel flexible industrial gas turbine applications. In the hopes of better understanding elemental variation effects on material properties, such as microstructural stability, castability, and heat treatability, a baseline composition referred to as the 'Model' alloy (based on CMSX-4 and PWA 1483) was used as the foundation from which two iterations of 'elemental variation effect' evaluations were conducted ('Phase I' and 'Phase II'). All alloy variations were submitted to and discussed with industrial collaborators (i.e., Siemens Power Corporation, Solar Turbines, Rolls-Royce and Howmet) The thermodynamic equilibrium module in the 3.0 Java-based Materials Properties Program (JMatPro) was utilized to evaluate 'Phase I' and 'Phase II' theoretical property trends and determine chemistry modifications to the baseline 'Model' alloy (Figure 1).

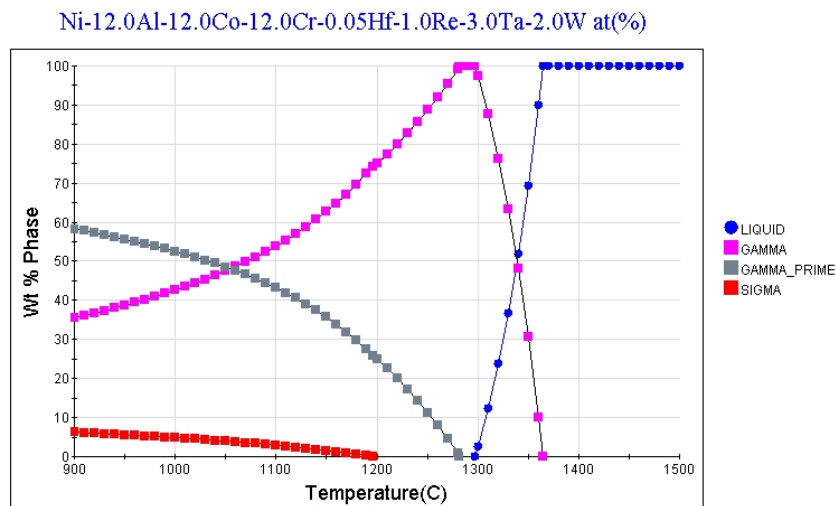


Figure 1 - Predicted phase fraction diagram for baseline Model alloy calculated by the JMatPro thermodynamic equilibrium module

All modeling work was completed at Siemens Power Corporation with extensive interaction between the University of Florida and Siemens Power Corporation. Based on the results of the Phase I and II predictions, five variant alloy compositions were tailored using JMatPro modeling techniques and were laboratory tested for validation purposes. To address the effects of additions previously shown to influence hot corrosion and material stability, final compositions incorporated characteristic variations of Al/Ti ratio (with Ta variation), Cr (with Al and Ta variations), and Re content for comparison. The results of the modeling and laboratory testing indicated that several of the alloy compositions had potential for IGT applications and will be processed using conventional techniques to further evaluate the potential of these alloys.

For clarity, the results of the two phases of computation studies are presented below. Elemental variation effects were investigated in the present study with the use of the JMatPro thermodynamic module for calculating material properties. In order to validate the calculated properties, five (5) alloys were selected and 50 gram buttons were arc-melted and characterized. The phase compositions, segregation behavior and phase transformation temperatures were determined for the five alloys. The results of the computational investigation of the 50 alloys and the five experimentally alloys, are grouped into common subject areas of Microstructural Stability, Phase Transformation Temperatures, Segregation and Elemental Variation Effects. The results are summarized as follows:

Microstructural Stability:

JMatPro microstructural stability modeling produced predictions that strictly apply to equilibrium conditions. However, the results can be applied to real non-equilibrium cases, as long as the kinetics of the formation of the topologically close-packed (TCP) phase is taken into consideration. In general, the alloys were ranked according to the predicted volume fraction of TCP phases present (Figure 2). All of the alloys had some TCP phases present, but trends were observed that indicated ways to reduce the predicted amounts of the deleterious phases. The results of the elemental variations are presented below.

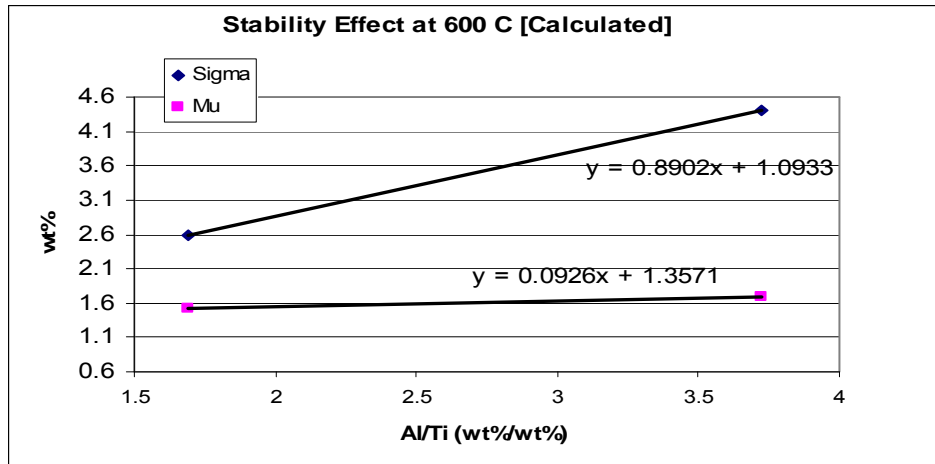


Figure 2 - Predicted Al/Ti ratio (and Ta) variation effects on TCP equilibrium phase amounts with respect to Al/Ti ratio.

In addition, the composition of the alloys was shown to have a significant effect on the composition and stability of the primary or MC-carbide. W concentrations in primary carbides contributed to MC degradation and dissolution during heat treatment. Ta concentrations in (Ti,Ta)C carbides contributed to maintaining MC stability during solution heat treatment.

Phase Transformation Temperatures:

JMatPro equilibrium calculations were not a viable tool in assessing accurate phase transformation temperatures for specific alloy compositions. Several of the final 5 alloys investigated in this study, exhibited transformation temperatures that were significantly different than those predicted by JMatPro (Figure 3).

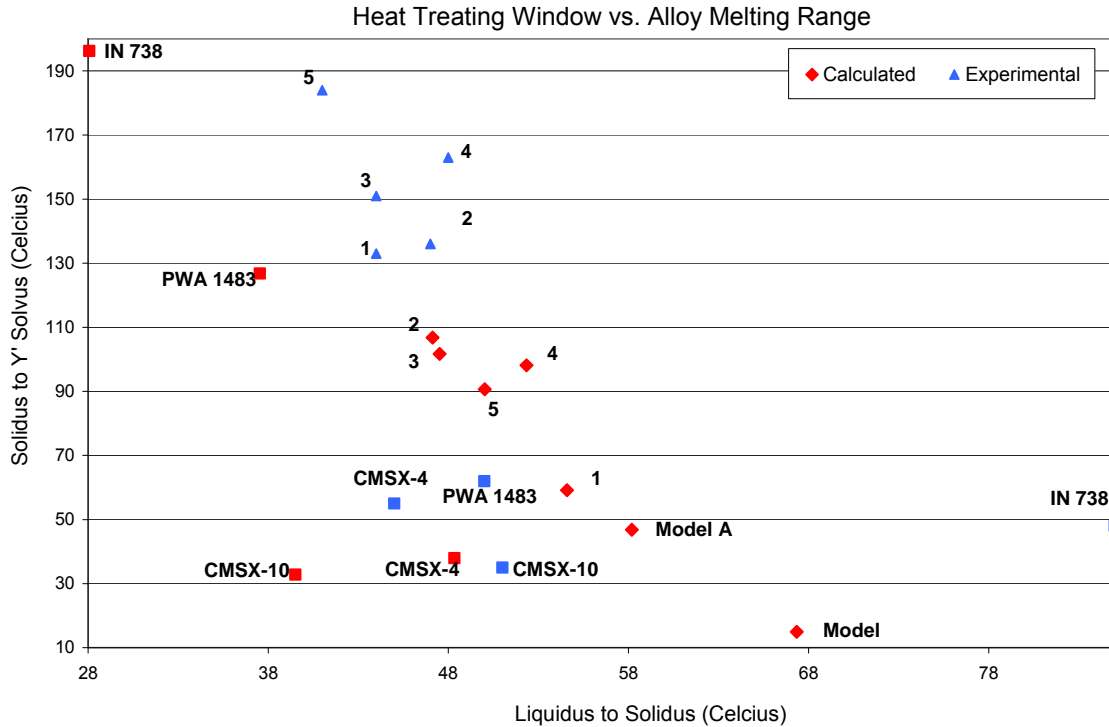


Figure 3 - Heat treatment window (solidus – γ' solvus) vs. melting range (liquidus – solidus) for the baseline Model composition, the baseline Model A composition, the compositional variants in 'Phase III', and selective 1st and 2nd generation commercial and experimental alloys

By applying equilibrium JMatPro calculations to IGT alloy design, five new IGT alloys were developed. All five alloys met the 25 °C target heat treatment window criteria

Segregation:

JMatPro proved to be a viable tool to determine qualitatively information on general elemental partitioning directions; either towards the dendrite core or the interdendritic region, based on comparison to literature data and on the results of the final phase of

this study. In the 'Phase III' compositions analyzed in this study, Ni, Co, W, and Re showed an overall tendency to partition to the dendrite core, while Ta, Ti, and Al tended towards the interdendritic region (Figure 4).

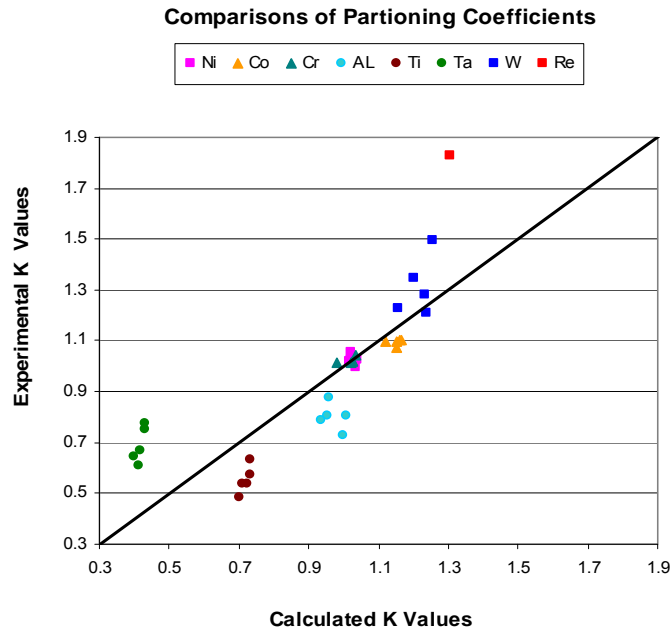


Figure 4 - Comparison between experimental and predicted partitioning coefficient values (k_{exp} vs k_{cal}) for 'Phase III' alloys

Elemental Variation Effects:

JMatPro equilibrium calculations successfully predicted general elemental trends in microstructural stability properties for C, Ti, Cr, Re, and γ' -former variations. It was also shown that JMatPro cannot be considered a viable tool to calculate Co, Ru, or W (Mo) variation effects on microstructural stability.

Carbon (C) additions were shown to increase microstructural stability; whereas, increased Ti, Cr, Re, and γ' -former contents decrease microstructural stability

JMatPro could be used to predict general Ta, Cr, W (and Mo), and γ' -former variation effects on phase transformation temperatures. JMatPro cannot be considered a viable tool to calculate C, Co, Ru, or Re variation effects on phase transformation temperatures. Ta concentrations increased the liquidus, solidus and decreased the γ' -solvus. Cr additions decreased the solidus and γ' solvus. Increasing W concentrations with corresponding Mo reductions increased the liquidus, and solidus temperatures. Increasing γ' -former content decreased the liquidus, decreased the solidus, and increased the γ' solvus. Increasing γ' -former content decreased the heat treating window.

Based on these results, alloy compositional effects could be identified that would produce an increased heat treating window and decreased melting range in the ultimate IGT alloys (Figure 4).

JMatPro equilibrium calculations successfully predicted general elemental trends in material segregation for γ' -former, Al (and Ta), Ti (and Al), Ti (and Ta), Al/Ti ratio, Cr, and Re variations. JMatPro calculations were not successful at establishing C, Co, or W (and Mo) trends for elemental segregation. Increasing γ' -former content increased elemental segregation. Al reductions with Ta substitutions increased material segregation. Ti additions used to substitute for Al reductions, decreased Re segregation while increasing W and Cr segregation. Ti additions used as a substitute for Ta reductions, increase W segregation and decreased Ni segregation. Increased Al/Ti ratios (with a Ta additions) decreased W segregation and increased Re segregation. Cr additions decreased segregation by decreasing the segregation of the heavy elements Re and W. Re additions increased elemental segregation.

Year 2:

Due the difficulties in utilizing the computation techniques to identify a new alloy composition for fuel flexible industrial gas turbine applications, another approach was utilized. In order to cast large IGT turbine blades, some alloy modifications have been reported to dramatically improve the castability of single crystal Ni-base superalloys. Small additions of boundary strengthening elements, such as C and B, have been shown to decrease the number of solidification defects and increase the defect tolerance of single crystal superalloys. In particular, several alloys based on CMSX-4 with small additions of C and B has been developed and are being considered for potential IGT applications.

Initially, carbon additions to single crystal alloys were reported to result in a significant reduction in solidification defects due to decreased segregation. However, more recent studies have shown that the reduced number of defects is due the presence of MC-type carbides restricting fluid flow during solidification. In addition, B and N additions have been reported to alter the morphology of the primary MC-type carbides in polycrystalline superalloys. The purpose of the current effort is to evaluate the ability to use computational techniques to model the experimentally determined data for single crystal Ni-base superalloys with the addition of C, B and N.

All alloy variations were submitted to and discussed with industrial collaborators (i.e., Siemens Power Corporation, Solar Turbines, Rolls-Royce and Howmet Research Corporation). The thermodynamic equilibrium module in the 3.0 Java-based Materials Properties Program (JMatPro) was utilized to evaluate the four CMSX-4-based alloy compositions (Table 1).

Table 1
 Target Composition of CMSX-4-based Alloys Investigated in this Study
 CMSX-4: Ni-9.6Co-6.5Cr-6.4W-0.6Mo-2.9Re-5.7Al-1.0Ti-6.5Ta-0.1Hf (wt%)

Alloy ID	Composition (wt%)			Comment
	C	B	N	
CMSX-4				Baseline
CMSX-4+C	0.05			
CMSX-4+C+B	0.05	0.005		
CMSX-4+C+N	0.05		0.0025	

All modeling work was completed at Siemens Power Corporation with extensive interaction between the University of Florida and Siemens Power Corporation.

For clarity, the results of the computation studies are presented first, followed by the experimental work. Elemental variation effects were investigated in the present study with the use of the JMatPro thermodynamic module for calculating material properties. The results of the computational investigation of the CMSX-4-based alloys are grouped into common subject areas of Phase Transformation Temperatures and Segregation. The results are summarized as follows:

Phase Transformation Temperatures:

JMatPro equilibrium calculations were used to calculate phase transformation temperatures for specific alloy compositions (Figures 5 thru 8). The liquidus, solidus and γ' solvus temperatures were calculated for all of the alloys and the MC-carbide (or M(C,N)-carbo-nitride) solvus was calculated for the alloys containing carbon (Table 2).

The addition of carbon to the CMSX-4 alloy resulted in the formation of MC-type carbides. These MC-carbides are rich in Ta and form between the solidus and liquidus temperatures. The carbon addition resulted in a slight reduction in all of the transformation temperatures (Figure 6). The addition of boron to the carbon containing CMSX-4 alloy composition was predicted to have only a small effect on the transformation temperatures. The CMSX-4+C+B alloy formed the MC-carbides and also formed boride phases (Figure 8). The addition of nitrogen to the carbon containing alloy was predicted to have a much greater impact on the phase transformation temperatures (Figure 8). The solidus temperature and the M(C,N)-nitride solvus temperature were predicted to increase. In particular, the M(C,N)-nitride solvus temperature was predicted to increase significantly from about 1358°C to 1631°C.

Ni-5.7Al-9.5Co-6.4Cr-0.1Hf-0.6Mo-2.9Re-6.5Ta-1.0Ti-6.3W wt(%)

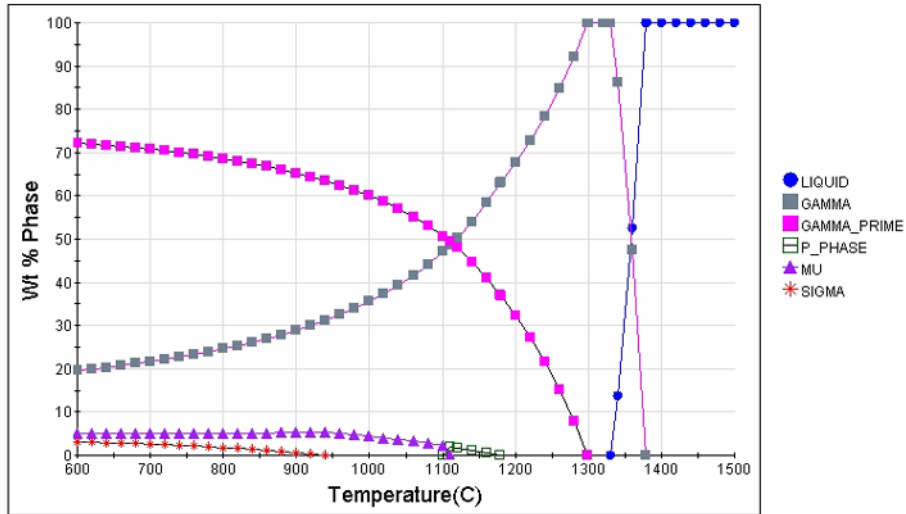


Figure 5 – Phase Diagram of CMSX-4 (baseline) alloy composition showing the amount (wt%) of the phases present versus temperature.

Ni-5.7Al-9.5Co-6.4Cr-0.1Hf-0.6Mo-2.9Re-6.5Ta-1.0Ti-6.3W-0.05C wt(%)

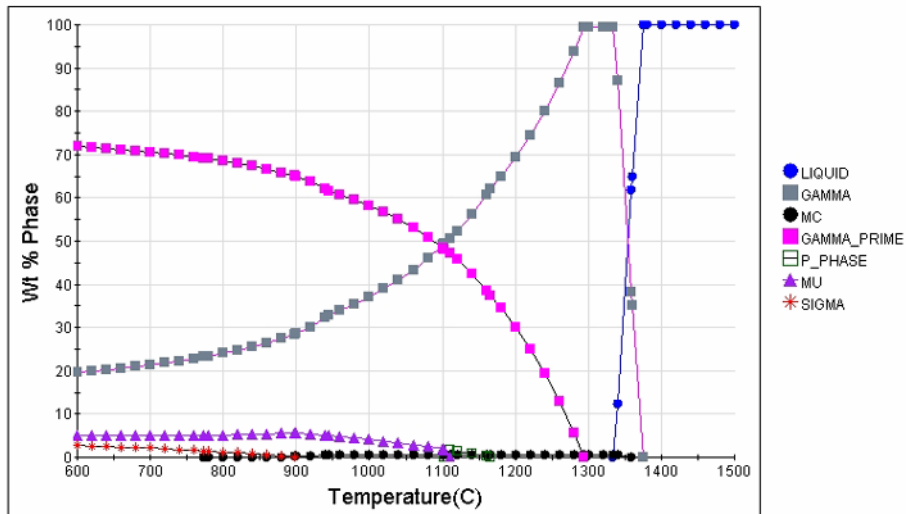


Figure 6 - Phase Diagram of CMSX-4+C alloy composition showing the amount (wt%) of the phases present versus temperature.

Ni-5.7Al-9.5Co-6.4Cr-0.1Hf-0.6Mo-2.9Re-6.5Ta-1.0Ti-6.3W-0.005B-0.05C wt(%)

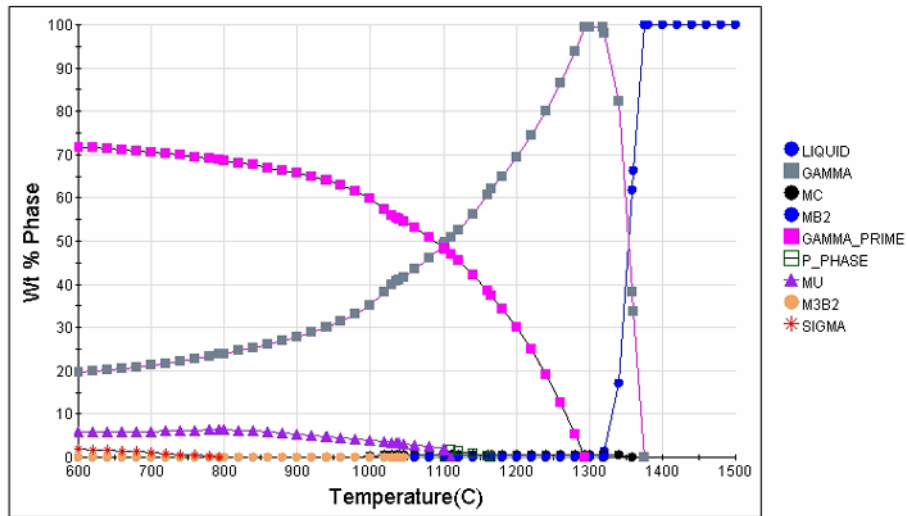


Figure 7 - Phase Diagram of CMSX-4+C+B alloy composition showing the amount (wt%) of the phases present versus temperature.

Ni-6.0Al-9.6Co-6.5Cr-0.1Hf-0.6Mo-2.9Re-6.5Ta-1.0Ti-6.4W-0.05C-0.0025N wt(%)

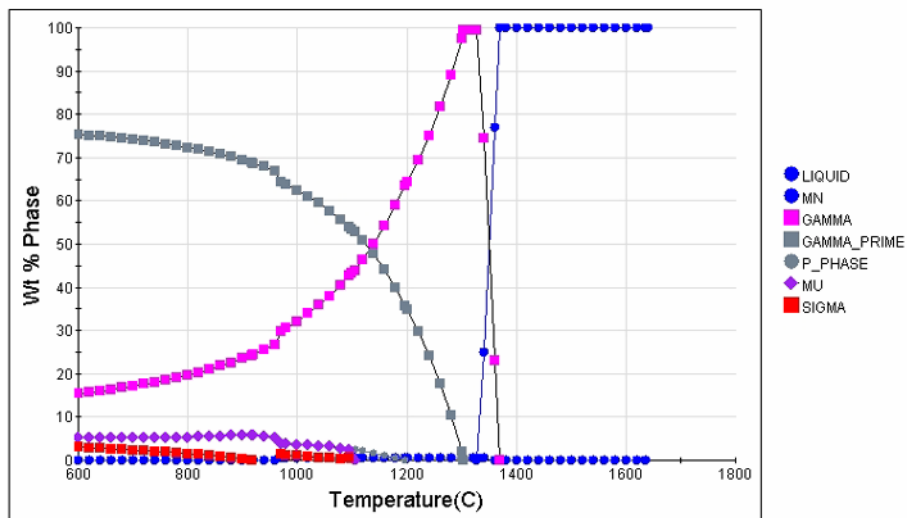


Figure 8 - Phase Diagram of CMSX-4+C+N alloy composition showing the amount (wt%) of the phases present versus temperature. Note that the addition of 0.0025wt% N₂ resulted in the stabilization of a TiN nitride phase to temperatures of approximately 1630°C

Table 2 – Phase Transformation Temperatures Predicted for the CMSX-4 Alloys

Alloy	Liquidus (°C)	Solidus (°C)	γ' -Solvus (°C)	MC-Carbide Solvus (°C)
CMSX-4	1379	1331	1299	NA
CMSX-4+C	1375	1319	1294	1358
CMSX-4+C+B	1375	1319	1293	1358
CMSX-4+C+N	1374	1332	1293	1631

Segregation:

JmatPro was used to predict the elemental partitioning during solidification. The composition of the first solid that forms at the liquidus temperature was determined and then divided by the nominal composition for each element. The elements that do not partition during solidification exhibit a partitioning ratio of 1. Elements that partition to the dendrite core exhibited a partitioning ratio greater than 1 and a partitioning ratio less than 1 indicates that the elements partition to the liquid (or interdendritic region).

Table 3 – Partitioning Coefficients Calculated for CMSX-4 Alloys

Alloy	Ni	Co	Cr	W	Mo	Re	Al	Ti	Ta	Hf
CMSX-4	1.02	1.09	0.94	1.15	0.87	1.57	0.89	0.73	0.47	0.11
CMSX-4+C	1.03	1.09	0.93	1.14	0.83	1.59	0.91	0.72	0.47	0.10
CMSX-4+C+B	1.03	1.09	0.93	1.14	0.83	1.59	0.91	0.72	0.47	0.10
CMSX-4+C+N	1.02	1.10	0.95	1.15	0.85	1.61	0.95	0.72	0.47	0.10

The coefficients calculated for the CMSX-4 indicated that partitioning coefficients were not a function of composition. The addition of carbon, boron and nitrogen did not have a significant effect on the partitioning coefficient.

Experimentally Determined Phase Transformation Temperatures

Cannon-Muskegon donated approximately 40Kg of CMSX-4 master alloy (from a single heat). One 10Kg heat of each alloy was processed at PCC Airfoils (Minerva, OH). Each mold consisted of twenty (20) 1.2cm diameter x 15 cm long cylindrical bars and were produced using conventional, high gradient casting techniques and commercial directional solidification furnaces. The bars were characterized for all types of defects and 250mg samples from each alloy were prepared for DTA analysis (Table 4). In addition, some DTA samples were evaluated after being given standard CMSX-4 homogenization heat treatments.

The heat treated DTA data would be expected to be more similar to the calculated phase transformation temperatures presented above (Table 2). However, both the as-cast and heat treated data are presented below. As seen in the previous progress

report, the calculated values for phase transformation temperatures were similar to the experimentally determined values in some cases, but in many cases, the magnitude of the changes in the phase transformation temperatures predicted and measured were quite different. For example, the boron additions were clearly seen to have a greater effect on the experimentally determined solidus temperature than predicted from the calculations. Furthermore, the addition of nitrogen did not result in a nitride solvus temperature that was significantly above the MC-carbide solvus temperature, as predicted by the JmatPro software.

Table 4 – Experimental Evaluation of As-cast and Heat Treated CMSX-4 Alloys.

	0.00C	0.05C	0.05C with boron	0.05C with nitrogen
Volume fraction eutectic (%)	12.0	8.1	6.3	8.1
Porosity volume fraction (standard deviation)	0.004 (0.002)	0.012 (0.006)	0.011 (0.004)	0.013 (0.005)
Primary arm spacing (μm)	299	383	309	302
DTA-as cast solidus (°C)	1319	1318	1316	1322
DTA heat treated solidus (°C)	1343	1339	1327	1340
DTA as cast liquidus (°C)	1386	1382	1382	1383
DTA heat treated liquidus (°C)	1389	1386	1384	1384
DTA as cast carbide (°C)	n/a	1369	1362	1367
DTA heat treated carbide (°C)	n/a	1369	1366	1369
Defects				
orientation	2/20	0/20	1/20	4/20
{HAB}	{0/20}	{0/20}	{0/20}	{4/20}
(LAB)	(2/20)	(2/20)	(1/20)	(1/20)
[sliver]	[1/20]	(1/20)	[1/20]	[1/20]
Defect free	15/20	17/20	17/20	12/20

Experimentally Determined Partitioning Coefficients

As-solidified samples were metallographically prepared and then examined using electron microprobe techniques to determine the partitioning coefficients. The results of this characterization are seen in Figure 9. The experimentally determined partitioning coefficients indicated that the addition of carbon had a relatively limited effect on partitioning, but the addition of boron and nitrogen both had appeared to reduce the segregation of several of the elements in the alloys.

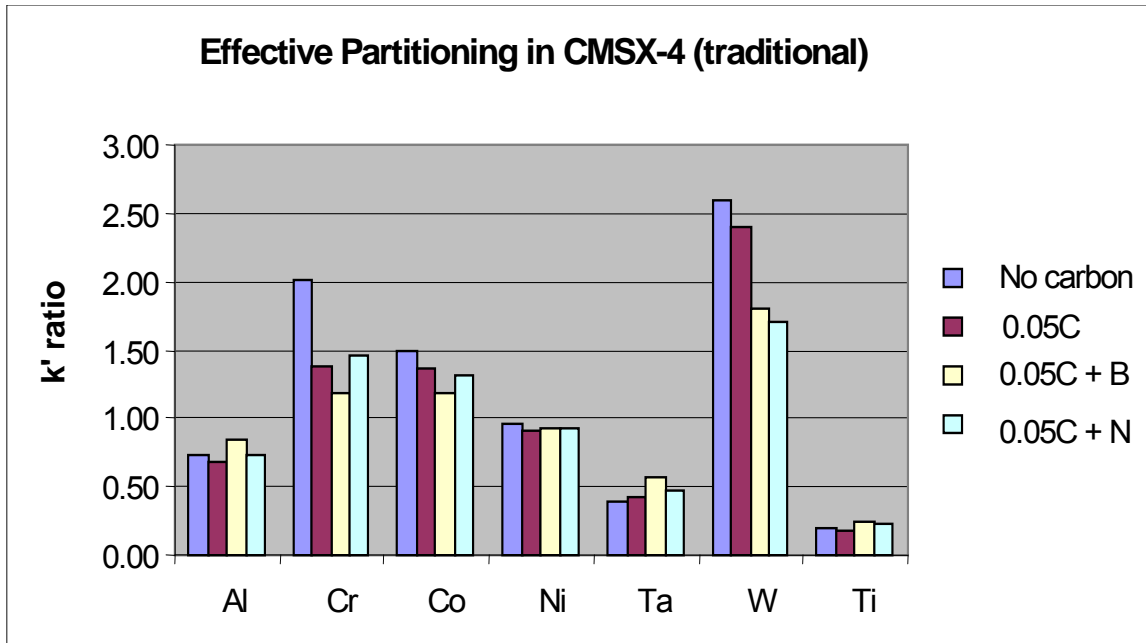


Figure 9 – Effective partitioning ratios of some of the elements in the CMSX-4 alloys. Note that the addition of carbon, boron and nitrogen appeared to have a much more significant effect on the partitioning of several of the elements in the alloy.

Year 3:

In Year 3, the calculation of the phase composition, segregation and phase transformation temperatures was completed and the effect of the C, B and N additions on the microstructures was characterized.

Carbon and boron, have been added to single crystal Ni-base superalloys to increase the yield and defect tolerance, but the effect of these additions on the solidification is not well understood. Carbon was added to the second generation single crystal Ni-base superalloy, CMSX-4, to form MC-type carbides. Nitrogen and boron were also added in an attempt to alter the carbide morphology.

The carbides were observed in the interdendritic regions, but were visible only at higher magnifications (Figure 10). At low magnification, all of the variations of CMSX-4 samples appear to have a similar microstructure. The change in dendrite morphology for the boron and nitrogen addition samples was observed only at higher magnifications. The addition of C to CMSX-4 resulted in a reduction in eutectic fraction, and the formation of carbides that precipitated between the secondary arms and, in some cases, appeared to block the development of some tertiary arms. The carbon and boron additions also exhibited a similar carbide structure. However, the carbides in the carbon + boron alloy were more blocky and irregular in shape and had a less uniform distribution. The addition of carbon also increased the PDAS (Table 2), similar to previous reports [4], due to the less regular structure of primary dendrite arms. However, the increased spacing was not seen in the two samples containing carbon and boron (C+B) and carbon and nitrogen (C+N).

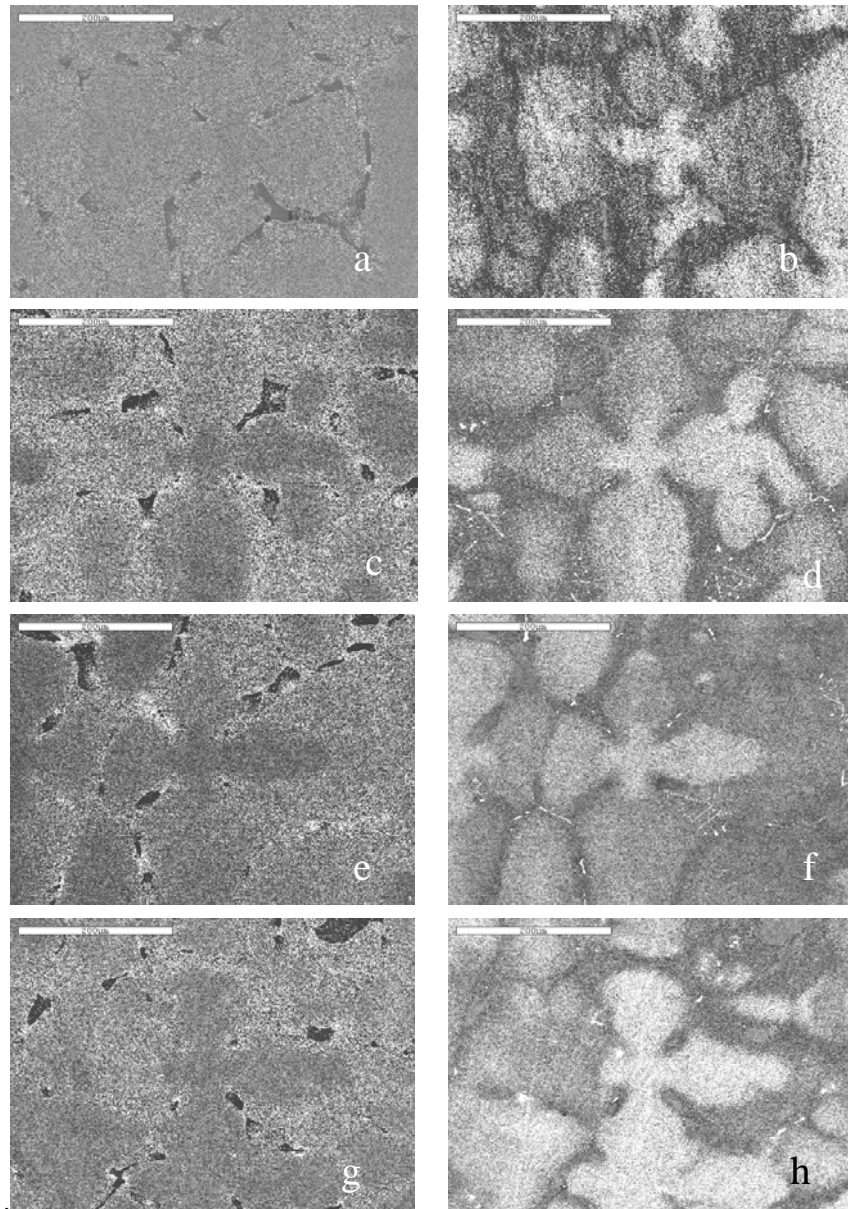


Figure 10 - SEM pairs of SE (left) and BSE (right) images. (a)(b) CMSX-4 (c)(d) CMSX-4 with 0.05C (e)(f) CMSX-4 with 0.05C and boron, (g)(h) CMSX-4 with 0.05C and nitrogen.

The addition of carbon to the alloy decreased the solidus and liquidus slightly in the DTA testing (Table 5). The addition of carbon and boron led to the largest reduction in the as-cast solidus. The boron-containing alloy also had the lowest carbide solvus in the as-cast condition. The transformation temperatures observed in the carbon and nitrogen alloy were very similar to those of the carbon only alloy. However, it should be noted that the differences in all of these transformation temperatures (Table 5) are limited due to the low level of the alloying additions used in this study. Furthermore, the carbide precipitation temperatures of the boron and nitrogen containing alloys are lower

than the carbon-only alloy, which indicates that the carbides in the boron and nitrogen containing alloys are forming lower in the mushy zone.

Table 5. As-cast data for CMSX-4 with alloying additions.

	Baseline	C	C+B	C+N
Volume fraction eutectic (%)	12.0	8.1	6.3	8.1
Porosity volume fraction (standard deviation)	0.004 (0.002)	0.012 (0.006)	0.011 (0.004)	0.013 (0.005)
Primary arm spacing (μm)	299	383	309	302
DTA as cast solidus, T_S ($^{\circ}\text{C}$)	1319	1318	1316	1322
DTA as cast liquidus, T_L ($^{\circ}\text{C}$)	1386	1382	1382	1383
DTA as cast carbide solvus, T_C ($^{\circ}\text{C}$)	n/a	1369	1362	1367
Melting Range, T_L-T_S ($^{\circ}\text{C}$)	67	64	66	61

Deep etching of longitudinal samples revealed differences between the dendritic carbide structures in the CMSX-4 variants (Figure 11). In the CMSX-4 with only the 0.05C addition, the carbides were observed to be interconnected networks of carbide sheets which grew in tandem with the dendritic structure. In the CMSX-4 sample containing carbon and boron, the carbides had a somewhat blocky morphology and do not extend as far into the interdendritic region as the carbides in the CMSX-4 with only carbon additions. In the CMSX-4 with carbon and nitrogen, the carbides were blocky, with a much smaller surface area. There was no evidence of nitrides forming either within or ahead of the mushy zone and acting as heterogeneous nucleation sites. All of these results are consistent with the transverse samples (Figure 10).

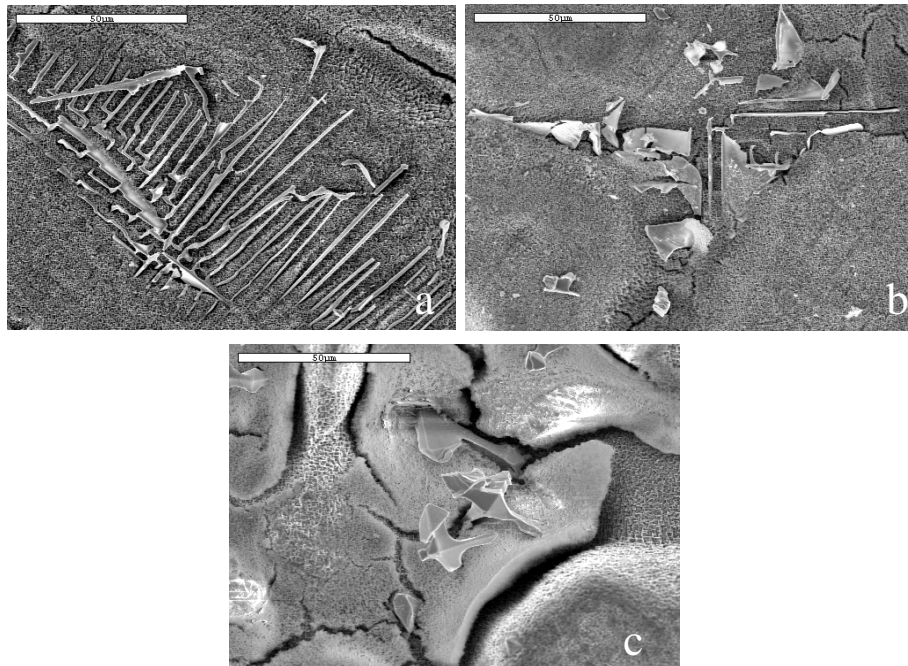


Figure 11 - Carbide shape of CMSX-4 variants compared. (a) 0.05C (b) 0.05C plus boron (c) 0.05C plus nitrogen.

The effect of carbides on the solidification of single crystal, Ni-base superalloys depends on several factors. In the production of directionally solidified Ni-base superalloys, typical withdrawal rates produce a dendritic structure with a “mushy” zone where solidification is taking place by the growth of dendrite arms both horizontally and vertically. The width of the mushy zone varies inversely with the thermal gradient. The precipitation temperature of the carbide determines the vertical location of the carbide in the mushy zone and, therefore, the fraction solid of the surrounding microstructure that can be associated with its formation. Carbides with higher precipitation temperatures precipitate higher in the mushy zone at a low fraction solid and therefore have a greater influence on the resulting microstructure.

The precipitation of tantalum carbides, the primary carbide observed in this study, has been shown to form at about 70% solid. The carbide solvus temperature obtained by DTA in this study correlates well with other work. No nitrogen was detected in the carbides in the nitrogen-containing sample due to the limited amount of nitrogen present in the alloy. Although the DTA data (Table 5) indicated a small difference in carbide precipitation temperature, EPMA analysis indicated that there was no substantial difference in the carbide composition between the carbon only, carbon and boron, and carbon and nitrogen additions. Since the boron and nitrogen containing alloys had lower carbide solvus temperatures than the carbon only alloy, the blocky carbide morphology in the boron and nitrogen containing alloys was not due to the previously reported mechanism of the carbides forming higher in the mushy zone. Perhaps the difference in carbide morphology was due to surface energy considerations due to small compositional differences of the carbide and/or the liquid in the mushy zone or some other mechanism (e.g., attachment) that controls the growth of the carbides.

Conclusions

Collaboration with Siemens Power Corporation (SPC), Rolls-Royce, Howmet and Solar Turbines identified and evaluated about 50 alloy compositions that are of interest for potential fuel-flexible IGT applications. In addition, alloy modifications to an existing alloy (CMSX-4) were also evaluated. Collaborating with SPC and using computational software at SPC to evaluate about 50 alloy compositions identified 5 candidate alloys for experimental evaluation. The results obtained from the experimentally determined phase transformation temperatures did not compare well to the calculated values in many cases. The effects of small additions of boundary strengtheners (i.e., C, B and N) to CMSX-4 were also examined. The calculated phase transformation temperatures were somewhat closer to the experimentally determined values than for the 5 candidate alloys, discussed above. The calculated partitioning coefficients were similar for all of the CMSX-4 alloys, similar to the experimentally determined segregation behavior. In general, it appears that computational materials science has become a useful tool to help reduce the number of iterations necessary to perform laboratory experiments or alloy development. However, we clearly are not able to rely solely on computational

techniques in the development of high temperature materials for IGT applications. A significant amount of experimentation will continue to be required.

Significant Accomplishments:

The material properties of several CMSX-4-based alloys, with potential IGT applications, were modeled successfully and included a significant amount of interaction between academia and industry. One phase of the work included laboratory verification/validation of computational predictions of several alloy compositions. The results of this work were used for the completion of a Ph.D. thesis and a M.S. thesis.