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ABSTRACT

Nickel base superalloys must be replaced if the demand for the materials continues to rise for applications beyond 1000°C which the upper limit for such alloys at this time. There are non-metallic materials available for such high temperature applications but they all present processing difficulties because of the lack of ductility. Metallic systems can present a chance to find materials with adequate room temperature ductility. Obviously the system must contain elements with high melting points. Nb has been chosen by many investigators which has a potential of being considered as a candidate if alloyed properly.

This research is exploring the Nb-W-Cr system for the possible choice of alloys to be used as a high temperature material. The ratio T/T_m for nickel based superalloys is 0.75 for 1000°C applications. This system shows solid phases up to 1500°C according to the published isothermal sections (Metals Handbook) from this ternary phase diagram. The choice of this present system is based on the following facts:

- a. Cr (7.19 gm/cm³) is the lowest melting point (1863°C) metal in this system.
- b. base metal Nb (melting point of 2468°C) has a density (8.57 gm/cm³) comparable to Ni (8.9 gm/cm³) based super alloys.
- c. W has a melting point of 3410°C and a density of 19.3 gm/cm³.
- c. all the 3 selected metals have a crystal structure of BCC.

Isothermal sections, from the Metals Handbook, of the ternary phase diagrams for Nb-W-Cr show that alloys can be held in solid state condition up to a temperature of 1500°C. The choice of compositions, Nb-20W-5Cr and Nb-20W-10Cr, was to test the oxidation resistance of the alloys when they are in single and 2 phase forms. There is a single phase, α , which is a solid solution of Cr and W in Nb present in both alloys but the second phase consists of NbCr₂, intermetallic compound known as laves phase, In turn this explores the enhancing capability of Laves phase to the oxidation resistance of the alloys from this system. Ames laboratory of Iowa State University was given the task of alloy fabrication and they used arc melting process in argon gas atmosphere to cast the alloys and the use EDM to produce desired dimensions. Usually a 5x5x5 mm disc samples were used for the oxidation studies.

The oxidation studies were conducted in two different ways. In the first method, the samples were heated for 24 hours at temperatures ranging from 700 to 1300°C and furnace cooled to room temperature. The weight gain per unit area was the experimental parameter that the measurable quantity used for estimating the oxidation resistance. The second method was devised so that more than one cycle of the first test method could be used. For example, a 14 cycles would indicate the heating period of 2 weeks in cycles of 24 hours. Again weight per unit area was the property indicative of the oxidation resistance. The testing temperature range was the same in both methods.

Initially research indicated that W was not very helpful in improving the oxidation resistance so it was decided to reduce its content from 20 atomic percent to 10 atomic percent. The effect of Cr was then determined by using alloys containing 15, 20, 25 and 30% Cr and 10%W in the same temperature range. However, a Pandat computer software program purchased recently indicated that 20W-5Cr alloy previously considered was not a single phase alloy but was a 2 phase alloys with NbCr₂ phase in low quantities until a temperature 1100°C. So the 2 phase microstructure stability was confirmed with this software for all of these newly developed alloys.

This report presents the results of oxidation studies on alloys containing varying amounts of Cr with 10%W. Details of the oxidation process were also evaluated by performing experiments involving less than 24 hours of heating. Another heating process was used where the alloys were continuously heated for extended periods of time compared to cyclic heating described above. The increased Cr concentration has been found to enhance the oxidation resistance but it is possible that this improvement may be associated with a limit on Cr content if W is to be held to 10%.

The compositional profiles to study the oxides formed at elevated temperatures will now be studied using XPS in AES in collaboration with our Physics department. Elemental compositional profiles can be used to estimate the types of oxides that may have formed. The results will be presented in a conference and attempt will be to publish them in a refereed journal later.

Maria Moricca is continuing for her Ph.D. dissertation on this topic and is nearing completion. Clemente Parga is a graduate student working on the Zr alloys but is studying the oxidation behavior at low temperatures (less than 600°C) only.

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7. RESULTS OF WORK

7.1 Approach

Alloys from Nb-W-Cr and Zr-Nb-Ti systems were fabricated by the Ames Laboratory (DOE) at Iowa State University. The alloys were received in the form of ½ inch square slices with 1/16th inch thickness.

7.1.1 Oxidation Experiments

- a. The alloys were subjected to oxidation in air in a range of temperature from 700 to 1400°C for alloys from Nb-W-Cr systems and 300 to 600°C for Zr-Nb-Ti systems using a computer temperature controlled furnace custom made by Applied Test Systems, Inc. (ATS).
- b. Oxidation of the samples was carried out using a ceramic crucible with a cap. The samples were held at the oxidizing temperature for 24 hours or 168 hours and were allowed to cool in the furnace up to room temperature.
- c. The weight gain/loss measurements were made using Sartorius Ag Gottingen balance having an accuracy up to six decimal places.

7.1.2 X-ray Diffraction

X-ray diffraction equipment made by Scintag Inc., (XDS 2000) was used to get the XRD patterns of the oxidized samples.

7.1.3 EDS on SEM

The oxide identification was also made using EDS on SEM (FESEM Hitachi 8700). Even though the output was in the form of elemental analysis, it is capable of estimating the stoichiometry of common oxides and/or compounds.

7.1.4 AEM and XPS

- a. The AEM (Phi 560 ESCA) was used to accurately conduct the surface elemental analysis while same equipment was used to sputter the surface in argon atmosphere for certain fixed periods of time.
- b. XPS was used to identify the near surface oxidized products.

7.1.5 Microstructural Characterization

- a. Optical microscopy was performed to identify the microconstituents after the exposure to air at specified temperatures.

- b. STEM was conducted using Hitachi 8000 scanning transmission electron microscope.
- c. TEM sample preparation was carried out by using either Tenupol-3 dual jet electropolisher or Gatan ion mill.

8. Results and Discussion

8.1 Isothermal Sections from Nb-W-Cr System

This research was initiated on the basis of the isotherms at 1000°C and 1500°C from Metals Handbook. The 1000°C isotherm indicated that Nb-20W-5Cr (20/5) alloy was a single phase alloy while Nb-20W-10Cr (20/10) alloy was a 2 phase alloy. Additionally, isothermal sections of the Nb-Cr-W phase diagram were calculated using a phase diagram calculation software for multicomponent systems, Pandat™ 7.0 provided by the CompuTherm LLC the software uses the most recent data from this system published thus far. Figure 1 compares the isotherms obtained from the two sources and do not match phase identification for the alloys used in this study. Even though the 20/10 alloy is a 2 phase alloy according to both sources, the 20/5 alloy which is a 2 phase alloy, as well, according to the Pandat 7.1 software program. Thus the assumption that the 20/5 alloy is a single phase alloys can not be used unquestionably.

Figure 1. Comparison of the isothermal sections from the Nb-W-Cr phase diagram from two different sources: (a) Metal Handbook and (b) Pandat 7.1 software.

Figure 2. Isothermal sections at 700 to 1400°C for the Nb-W-Cr System calculated using Pandat 7.1 Software.

Figure 2 shows the isothermal sections at 700 to 1400°C in an increment of 100°C from the Nb-W-Cr phase diagram. It must be noted that 20/5 alloy is a 2 phase alloy until 1000°C but then falls almost on the solvus line separating the single phase (α) alloy from that of two phase region consisting of α and NbCr₂. This software predicts that 20/5 alloy is in a single phase region at all temperatures above 1000°C. However, the 20/10 alloy is a 2 phase alloy at all temperatures of this study according to both sources. It must be noted that, even though the present compositions are not affected by this observation, the single phase NbCr₂ region appears to be present when 20/5 alloy transforms from two phase to single phase alloy at approximately 1100°C.

8.2 Microstructural Verification of Phase Prediction from Pandat 7.1 Software

Figures 3, 4, and 5 show the actual microstructures of the 20/5 and 20/10 alloys after heating for one hour in air at 700, 1000 and 1100°C. The 2 phase microstructures in both alloys at 700°C can be seen in Figure 3 and the composition of the Laves phase has been verified by the EDS on SEM. The 2 phase microstructure can be observed in both alloys at temperatures as high as 1000°C as indicated in Figure 4 which presents a comparison between both 20/5 and 20/10 alloys along with EDS analysis of the laves phase. The intermetallic phase is mainly present along the □ grain boundary. The 2 phase microstructure can no longer be observed in the 20/5 alloy after the heat treatment at 1100°C as indicated by Figure 5.

A comparison of the microstructures from alloys oxidized at 700, 1000 and 1100°C clearly shows that the 20/5 alloy becomes single phase while 20/10 alloy remains 2 phase at 1100°C. The amount of laves phase that is detectable experimentally in the 20/5 alloy dramatically decreases as temperatures approach 1100°C as indicated by the theoretical data presented in Table 1. A comparison of the microstructure observed after the heat treatments at 1000, 1100, and 1200°C is presented in Figure 6 to collaborate with the data presented in Table 1.

Figure 3. Comparison of the Microstructures developed in (a) 20/5 and (b) 20/10 alloys after heating at 700°C for one hour.

Figure 4. Microstructures developed in (a) 20/5 and (b) 20/10 alloys after heating at 700°C for one hour. The EDS analysis on the BSE for a Laves phase is indicated in (c).

Thus it can be speculated that the Pandat 7.1 provides the more realistic description of the microstructures. The enhancement of oxidation resistance by the Laves phase can

Figure 5. Comparison of the Microstructures developed in (a) 5/20 and (b) 10/20 alloys after oxidation at 1100°C for one hour.

Table 1. Fractions of the phases present in 5/20 and 10/20 alloys at different temperatures according to Pandat™ program.

Alloy Temperature	5/20 Alloy		10/20 Alloy	
	α	NbCr ₂	α	NbCr ₂
700	0.89	0.11	0.75	0.25
800	0.91	0.09	0.77	0.23
900	0.93	0.07	0.78	0.22
1000	0.95	0.05	0.80	0.20
1100	0.98	0.02	0.82	0.18
1200	1.0	0	0.85	0.15
1300	1.0	0	0.89	0.11
1400	1.0	0	0.93	0.07

thus be accepted based on the actual experimental observations of this study. Literature supports that NbCr₂ provides the oxidation resistance in this Nb-W-Cr system.

5/20 Alloy

10/20 Alloy

1100°C

1100°C

1200°C

1200°C

Figure 6. Microstructures developed in 5/20 and 10/20 alloys after heating at 1000, 1100, and 1200°C for one hour.

8.3 Effect of B and C additions on A and B alloys (20/5 and 20/10)

8.3.1 As Cast Structures

A and B alloys containing Boron or Carbon are designated as AB, AC and BB, and BC alloys. Figure 7 shows the microstructures of the alloys in the as cast condition. Grains of a solid solution of Cr and W in Nb form α phase in each case. NbCr₂ intermetallic can also be recognized in the 20/10 alloys. According to microstructure comparison, the addition of 0.1 weight percent of C and B boron do not alter the microstructures in any noticeable manner.

Figure 7. Micrographs of the alloys A, B, AB, BB, AC and BC in the as cast condition.

The XRD patterns obtained from the as cast structures of the alloys A, AB, AC and B, BB, BC are shown in Figure 8. The phases were identified by matching the characteristic XRD peaks against JCPDS (Joint Committee for Powder Diffraction Standards) files. The peak identification shows the presence of Nb solid solution (α), the percentage of the Laves phase and carbon and boron modifiers is apparently too low to be identified. The dashed lines in Figure 8 represent the diffraction positions of the pure niobium (JCPDS 34-370); the Nb_{ss} peaks are shifted to the right of the intensity peaks expected for pure niobium, suggesting that the Nb_{ss} phase has a reduced lattice parameter compared to pure Nb. Decrement in the lattice parameter is in accordance with the smaller atomic radii of W (1.371Å) and Cr (1.249Å) compared to Nb (1.426 Å) if it is assumed that W and Cr form a substitutional solutions with Nb.

Figure 8. XRD patterns of the as cast alloys A, AB, AC, B, BB, and BC.

8.3.2 Short Term Oxidation (24 Hours), STO

Figures 9 and 10 show the variations in weight gain per unit area as a function of oxidation temperature for 24 hour exposure (STO) to air for the six alloys of this study. The curves indicate the presence of solid-powder (SP) mixture at 700°C, mainly powder (P) at 800°C, 900°C, and 1000°C, SP forms at 1100°C and 1200°C, and solid (S) forms at 1300°C, and 1400°C for all alloys. Consistent lower weight gain for AC alloy at

temperatures above 900°C can be seen in Figure 9. This indicates that the carbon modifier in the alloy is beneficial for the enhancement of oxidation resistance of alloy A. This alloy also shows better oxidation resistance compared to AB alloy except at 1000°C and 1100°C. High oxidation resistance of AC alloy is noteworthy.

Figure 10 shows the SP, P, SP and then S forms of the oxidized products in a similar temperature range for B alloys as is shown in Figure 9 for A alloys. However, neither boron nor carbon additions have been found to have beneficial effect on the oxidation resistance of B alloy. Comparison between the oxidation curves for BB and BC alloys indicates that the BC alloy is superior at and above 1200°C.

Figure 9. Oxidation curves for the alloys A, AB, and AC after 24 hour exposure to air from 700 to 1400°C.

The powder formation observed in the intermediate temperature range may be explained on the basis of the thermal linear expansion (TLE, an indication of the coefficient of thermal expansion, CTE) values of the oxides as shown in Table 1 and the nature of WO_3 formation.

It has been reported that W begins to volatilize at 750°C in the presence of moisture even from the atmosphere. Table 1 shows that TLE values are many orders of magnitude higher for WO_3 compared to Nb_2O_5 and are nearly double compared to those for Cr_2O_3 .

Figure 10. Oxidation curves for the alloys B, BB, and BC after 24 hour exposure to air from 700 to 1400°C.

Table 1. Comparison of Thermal Linear Expansion Values of Oxides

Oxide	Thermal Linear Expansion (%)			
	700°C	800°C	900°C	1000°C
Nb ₂ O ₅	0	0.02	0.04	0.07
Cr ₂ O ₃	0.54	0.60	0.68	0.76
WO ₃	0.98	1.02	1.14	-

The simultaneous formation of the three oxides can result in cracking and depending on the extent of reactions it can result in the formation of complete powders. It must be pointed out that the complete powder formation in its finest form has been observed for all 6 alloys of this study at 800°C.

8.3.2.1 XRD of Oxidation Products

Figures 11 and 12 show the XRD patterns of the oxidation product for alloys AB, AC, BB, and BC at different temperatures. There are no detectable differences in the peaks indexed at all the temperatures. Basically they confirm that Nb₂O₅, Cr₂O₃, WO₃, and CrNbO₄ are the main constituents.

It must be noted that Cr₂O₃ vaporizes at temperatures above 1000°C according to many investigators. It is possible to observe the Cr₂O₃ peak in the powder patterns of the

oxide scale, obtained at higher temperatures, if it is assumed that vaporization can also result in its entrapment in the scale.

Figure 11. XRD spectra of the oxidation products obtained after oxidation for 24 hours in air for alloys AB and AC.

Figure 12. XRD spectra of the oxidation products obtained after oxidation for 24 hours in air for alloys BB and BC.

8.3.2.2 SEM of Surface Oxides

Figure 13 shows the comparison of the morphological nature of the oxides formed at the surface of the alloys AB and AC, respectively, while Figure 14 indicates similar comparison for BB and BC alloys, respectively. SEM pictures taken at similar magnifications attest to the fact that there is considerable coarsening of the oxides with an increase in oxidation temperature. The geometrical shapes of the oxides seen in these micrographs correspond to either globular (more or less spherical) and elongated or cylindrical types. The EDS on SEM analyses indicate that the longitudinal shapes are depleted of Cr.

The globular types show the almost depletion of W but contain Nb, Cr, and O in the ratio of 1:1:4 which will indicate the formation of ternary oxide NbCrO_4 during the oxidation sequence. It has been reported in the literature that this oxide serves as a protective layer and enhances the oxidation resistance of the alloy. It can result from the oxidation of the intermetallic compound NbCr_2 and/or two moles of Nb_2O_5 and Cr_2O_3 can combine to form the NbCrO_4 . Both options are considered to be highly speculative.

Figure 13. SEM images of surface morphologies of alloys AB, and AC after oxidation at 1200°C and 1400°C.

Figure 14. SEM images of surface morphologies of alloys BB, and BC after oxidation at 1200°C and 1400°C.

8.3.3 Cyclic Oxidation Experiments

Isothermal experiments were performed to elucidate the effect of number of 24 hour cycles on the weight gain/area. These experiments were performed by periodic removal of a specimen, weighing and re-insertion for further exposure at constant temperature. Different samples of the A, B, AC and BC alloys were heated for 1 and 4 hours and then in 4 hours intervals up to 24 hours and cooled in the furnace to room temperature. Figure 15 shows the weight gain per unit area as a function of oxidation time at 1300°C. The behavior exhibited by these alloys may be considered as a 2-stage oxidation process, the time at which the oxidation rate stabilizes depends on the alloy composition. The initial oxidation behavior shows that B alloy has better oxidation resistance than A alloy indicating the beneficial effect of the presence of intermetallic compound in the microstructure. The effect of C as a modifier shows better response in improving the resistance of AC alloy in comparison to BC alloy. The curves tend to stabilize for all the alloys to approximately similar weight gain/area values.

Figure 15. Isothermal oxidation curves for alloys A, B, AC and BC at 1300°C.

8.3.4 Long Term Oxidation (168 Hours), LTO

Figures 16 to 21 show the variations in weight gain per unit area as a function of oxidation temperature for 168 hours exposure (LTO) to air for the six alloys of this study. The curves exhibit a consistent lower weight gain for AC and BC alloys, indicating that the carbon modifier in the alloy is beneficial for the enhancement of oxidation resistance of alloys A and B. A significant change in the oxidation kinetics of the alloys containing the B modifier is not observed when compared to the unmodified alloys.

Figure 16. Oxidation curves for the alloys A, AB, and AC after 168 hours exposure to air at 1200°C.

Figure 17. Oxidation curves for the alloys B, BB, and BC after 168 hours exposure to air at 1200°C.

Figure 18. Oxidation curves for the alloys A, AB, and AC after 168 hours exposure to air at 1300°C.

Figure 19. Oxidation curves for the alloys B, BB, and BC after 168 hours exposure to air at 1300°C.

Figure 20. Oxidation curves for the alloys A, AB, and AC after 168 hours exposure to air at 1400°C.

Figure 21. Oxidation curves for the alloys B, BB, and BC after 168 hours exposure to air at 1400°C.

8.3.4.1 SEM of surface Oxides

Figures 22 and 23 are secondary electron images of the oxidized surface of the alloys AB, AC, BB, and BC alloys at 1200⁰C, 1300⁰C and 1400⁰C. Images do not show considerable coarsening of the oxides with an increase in oxidation temperature as observed for STO samples, with the exception of BC sample that exhibits few areas containing smaller spheres as shown in Figure 22. The geometrical shapes of the oxides seen in these micrographs correspond to either globular (more or less spherical) and elongated or cylindrical types. According to the EDS analysis performed, the longitudinal shapes exhibit a stoichiometry that may correspond to Nb₂O₅. The small globular shapes from sample BC1200 exhibit W depletion but contain Cr in higher amounts when compared to longitudinal shapes. Elemental composition analysis indicates that the W content decreases as temperature increases, products obtained at 1400⁰C show almost W depletion, suggesting that the oxide Nb₂O₅ is the main constituent at this temperature.

The XRD analysis performed on oxidation products showed no detectable differences between the patterns at the three temperatures. Peak identification indicates that Nb₂O₅, Cr₂O₃, WO₃, and CrNbO₄ are the main constituents of the products.

Figure 22. SEM of the oxidized surfaces at 1200, 1300, and 1400°C for the AB and AC alloys after LTO.

Figure 23. SEM of the oxidized surfaces at 1200, 1300, and 1400°C for the BB and BC alloys after LTO.

8.4 Effect of Cr content on oxidation behavior

8.4.1 As Cast Structures

Alloys with 15, 20, 25, and 30%Cr were used to determine the effect of Cr on the oxidation behavior; the alloys have been identified as E, C, F, and D respectively. The W concentration has been reduced from 20% to 10% since it has been found that significant amount of W was lost due to volatilization in the atmospheric moisture when heated at around 750 to 800°C.

BSE images of 15Cr, 20Cr, 25Cr, and 30Cr alloys in the as-cast condition are presented in Figure 24. Microstructure of alloys consists of Nb solid solution phase regions and the intermetallic NbCr₂ laves phase, an increase of the intermetallic phase is observed as the Cr content increases.

Figure 24. BSE images of 15, 20, 25, and 30%Cr alloys in the as cast condition.

The XRD patterns obtained from the as cast structures are shown in Figure 25. Individual phases and their crystal structures were identified by matching the characteristic XRD peaks against JCPDS files. The peak identification confirms the presence of two phases, Nb solid solution (α) and the cubic type (C15) laves phase

NbCr₂. The dashed lines in Figure 25 represent the diffraction positions of the pure niobium (JCPDS 34-370); the Nb_{ss} peaks are shifted to the right of the intensity peaks expected for pure niobium, suggesting that the Nb_{ss} phase has a reduced lattice parameter compared to pure Nb. As the Cr concentration increases the intensity of the intermetallic compound peaks increases, which at this point can be qualitatively related to the amount of intermetallic phase in the alloy.

Figure 25. XRD patterns of 15, 20, 25, and 30Cr alloys in the as cast condition.

8.4.2 Short Term Oxidation (STO)

A comparison of the oxidation curves obtained after 24 hours exposure in air for a range of temperatures from 700°C to 1400°C is shown in Figure 26. The oxidation behavior can be described in stages. Initially the weight gain per unit area (w/a) increases with increase in temperature for all the alloys up to 900°C. A nearly constant weight gain is observed from 900°C to 1100°C for alloys with lower Cr content (15Cr and 20Cr); and in the case of alloys 25Cr, and 30Cr the constant weight gain continues up to 1300°C, delineating the superior oxidation behavior of alloys with higher Cr. At 1400°C the

weight change on samples 15Cr and 20Cr appears to stabilize compared to the change on samples 25Cr and 30Cr which is now significantly higher, a systematic behavior with respect to Cr content could not be established at this temperature.

Figure 26. Comparison of oxidation curves for alloys after 24 hours exposure in air.

According to the oxidation behavior observed at different temperatures and the ranges identified, detailed oxidation experiments at 800°C, 1100°C, and 1300 °C were conducted in order to determine the different stages of the oxidation process as well as the relation with the intermetallic phase content.

The isothermal oxidation curves at 1300°C for the alloys with 15%Cr (E), 20%Cr (C), 25%Cr (F), and 30%Cr (D) are shown in Figure 27. The oxidation kinetics closely follows parabolic behavior. The curves delineate the beneficial effect of the Cr additions. Alloys with lower Cr content show higher weight gains in the initial stage but the change becomes smaller after initial oxidation. Alloys 25Cr and 30Cr exhibit comparable oxidation behavior during the 24 hour exposure. The large weight gain for alloys 15Cr and 25Cr and the small weight gain for alloys 25Cr and 30Cr suggest the existence of a limit concerning the effectiveness of Cr contribution to oxidation resistance.

Figure 27. Isothermal oxidation of alloys 15Cr, 20Cr, 25Cr, and 30Cr at 1300°C.

Cyclic oxidation experiments were performed to elucidate the effect of time during the 24 hours of heating period. These experiments were performed by periodic removal of a specimen, weighing and re-insertion for further exposure at constant temperature. The alloys were heated for 1 and 3 hours and then in 4 hours intervals up to 24 hours and cooled in the furnace to room temperature. Figure 28 shows the mass gain per unit area as a function of oxidation time at 1300°C. The behavior exhibited by these alloys may be considered as a 2-stage oxidation process, the time at which the oxidation rate stabilizes depends on the alloy composition. The oxidation behavior shows that the 30Cr alloy has the best oxidation resistance; the oxidation curves also indicate that alloys with concentration higher than 25% Cr show a significant improvement on oxidation resistance when compared to alloys containing 20% Cr or lower.

Figure 28. Isothermal oxidation curves for 15Cr, 20Cr, 25Cr, and 30Cr alloys at 1300°C using cyclic experiments.

For isothermal exposures the rate of oxidation determines the rate of material consumption. The analyzed samples exhibited reduced oxidation rates during static oxidation compared to cyclic oxidation which is expected due to scale spallation occurring during cooling, resulting in loss of the protective oxide layer. The alloy will experience accelerated oxidation in the spalled regions because of the inverse growth rate dependence upon thickness.

8.4.2.1 Oxidation Products Characterization

Figure 29 is a secondary electron image of a 30Cr sample oxidized for 24 hours at 700°C. The scale is layered and grows preferentially at the edges; these features have been previously reported by several authors. EDS analysis indicates that the outer layers are W rich and its concentration decreases towards the base metal. Table 2 summarizes the results obtained from the elemental analysis performed on oxide layers.

Figure 29. SEM image of oxide scale on sample 30Cr oxidized at 700°C for 24 hours.

Table 2. Elemental composition of oxide layers of sample 30Cr oxidized at 700°C for 24 hours.

Area	wt%				at%			
	Nb	Cr	W	O	Nb	Cr	W	O
A	5.1	3.2	78.5	13.2	4.0	4.4	31.2	60.4
B	8.4	5.4	78.5	7.7	8.2	9.4	38.8	43.6
C	29.3	24.3	26.0	20.4	14.4	21.3	6.4	57.9

Figures 30 and 31 show the microstructures of samples 20Cr and 30Cr alloys after oxidation at 1000 and 1200°C for 24 hours respectively. The intermetallic phase which is a continuous phase in this case retains its structure which implies that oxidation reaction with Nb, W, and Cr occurs from the locations containing α phase.

Oxide Surface

Metal

Oxide-Metal Interface

Figure 30. SEM images of alloy 20Cr oxidized at 1000°C and 1200°C showing the morphology of the oxidized surface, metal matrix, and the oxide-metal interface.

Oxide Surface

Metal

Oxide-Metal Interface

Figure 31. SEM images of alloy 30Cr oxidized at 1000°C and 1200°C showing the morphology of the oxidized surface, metal matrix, and the oxide-metal interface.

Figure 32 presents BSE images of a cross-section of a 30%Cr sample oxidized at 1300°C for eight hours. The outer oxide scale was partially spalled; Cr content at spalled oxide is lower and the oxide is Nb and W rich indicating that the spalled region is a

combination of Nb and W oxides. The sample exhibits compositional changes as well as microstructural changes, the EDS analysis indicates that W content slightly increases toward the edge. The particles observed at Nb solid solution areas exhibit a composition similar to the intermetallic NbCr₂ phase.

Figure 32. BSE images of cross-section of sample 30Cr oxidized at 1300°C for 8 hours.

The oxidation products of the different alloys were identified by XRD. The XRD pattern obtained from oxidation products of sample 30Cr oxidized at 1300°C during 24 hours (cyclic) is presented in Figure 33. The product was identified as CrNbO₄ (JCPDS 34-0366).

Figure 33. XRD patterns for oxidation products from sample 30Cr after cyclic oxidation (7 cycles) for a total of 24 hours.

8.4.3 Long Term Oxidation (LTO)

In order to determine the relationship between alloy composition and oxidation products, the samples were oxidized for a total of 168 hours using 24 hour intervals. The oxidation products in powdered form were characterized by XRD.

Figure 34 shows the long term oxidation (168 hours or one week) curves for alloys 15Cr, 20Cr, 25Cr, and 30Cr (containing 10%W) when exposed to a temperature of 1300°C in air. The process can be described in two stages. The first stage shows an increase in weight gain per unit area as a function of oxidation time. The second stage basically consists of stabilization of weight change values which in this case indicates the oxidation of the complete samples while the first stage retains the metals with various forms of oxidation products. The LTO curves show an increase in oxidation resistance with an increase in Cr concentration. It is presumed that the increased proportion, Table 2, of the intermetallic compound, NbCr_2 , with increase in Cr is responsible for the improved oxidation resistance.

Figure 34. Long term oxidation (LTO) curves for the 15, 20, 25, and 30%Cr alloys exposed to air at 1300°C for a period of one week or 168 hours.

Figure 35 presents the XRD patterns of oxides obtained from samples 15Cr, 20Cr, 25Cr, and 30Cr after 168 hours cyclic exposure. The oxides identified are CrNbO_4 , Nb_2O_5 , and Cr_2O_3 . As the Cr concentration increases the intensity of the Nb_2O_5 , and Cr_2O_3 compounds peaks decreases; CrNbO_4 is the predominant oxide in sample 30Cr.

Figure 35. XRD pattern of the oxidized products obtained from the 4 alloys after 168 hours of exposure at 1300°C.

The improved oxidation resistance is clearly marked by the increase in brittleness in the alloy. This can be a major thrust required for the development of the alloy for the high temperature applications. The improvement in ductility through various thermo-mechanical methods is beyond the scope of this proposed research. But it is definitely something that can be explored in the future if the compositional changes permit the use of these alloys at least for oxidation resistance purposes.

Table 2 Fraction of phases present in Cr alloys at different temperatures according to Pandat™ 7.0

°C	C(15Cr)		E(20Cr)		D(25Cr)		F(30Cr)	
	□	NbCr ₂	□	NbCr ₂	□	NbCr ₂	□	NbCr ₂
25	0.62	0.38	0.52	0.48	0.42	0.58	0.32	0.68
900	0.68	0.32	0.56	0.44	0.45	0.55	0.35	0.65
1100	0.72	0.28	0.59	0.41	0.47	0.53	0.36	0.64
1300	0.78	0.22	0.64	0.36	0.51	0.49	0.39	0.61

SUMMARY

A, AB, AC, B, BB, and BC alloys

The alloys containing higher Cr concentration exhibit enhanced oxidation resistance. Increasing exposure time, temperature, or both, resulted in oxide growth leading to thicker oxides with particle coarsening.

Alloy microstructure consisted of primary Nb solid solution phase regions surrounded by a network of the NbCr₂ laves phase.

Boron additions were found to cause chromium segregation at grain boundaries and precipitate boundaries in AB alloy to an extent where compositions after the argon heat treatment were comparable to those measured for the laves phase found in the B series of alloys.

The oxidation products of the alloys at temperatures from 800°C to 1400°C are a mixture of Nb₂O₅, WO₃, Cr₂O₃, and CrNbO₄. The nature of oxides in monolithic form and with B and C additions has been observed to be similar based on the XRD results

The alloys A, B, AB, BB, AC, and BC exhibit complete powder formation after oxidation at 800°C and 900°C. The behavior may be attributed to the large differences in the linear thermal expansion of the oxides, particularly WO₃.

Beneficial effects have been observed when C is added to A alloy; however alloy B shows degradation of the oxidation resistance by the addition of any of the modifiers. Long term oxidation data indicates the addition of boron is detrimental to the modified alloys oxidation resistance.

Results obtained from alloys A and B indicate that concentrations containing 20% tungsten are detrimental for the formation of a protective layer.

15Cr, 20Cr, 25Cr, and 30Cr Alloys

The oxidation kinetics follows a parabolic behavior and the time at which the oxidation rate stabilizes is alloy composition dependent. Alloys with higher Cr concentration exhibit enhanced oxidation resistance, which at this point could be related to the amount of intermetallic phase on the alloy.

Mass gain values obtained at 1300°C for alloys identified as F (25Cr) and D (30Cr) are competitive compared to the values for Nb-based alloys reported by different authors.

The oxidation products of the alloys are a mixture of CrNbO_4 , Nb_2O_5 , and Cr_2O_3 . As the Cr concentration increases the intensity of the Nb_2O_5 , and Cr_2O_3 compounds peaks decreases; CrNbO_4 is the predominant oxide in sample 30Cr.

The alloys containing higher Cr concentration exhibit enhanced oxidation resistance. Increasing exposure time, temperature, or both, resulted in oxide growth leading to thicker oxides and particle coarsening.

The results obtained delineate the complexity of the oxidation mechanism and the influence of microstructure and composition of these alloys.

9. ACCOMPLISHMENTS

The ternary isothermal sections obtained from Metals Handbook and Pandat software program appear to contradict each other. Handbook shows 20W-5Cr alloy to be a single phase alloy but the Pandat software indicates that it can be 2 phase alloy up to a temperature of 1100°C. In fact this has allowed us to interpret that NbCr_2 phase is the micro constituent that enhances oxidation resistance in these alloys. This was based on the fact that 5Cr alloy becomes single phase at temperature above 1200°C and loses its oxidation resistance capability considerably.

The effect of Cr concentration on the oxidation resistance for the alloys containing 10%W has been found to be beneficial. Clearly the alloys containing higher Cr contents show lower weight gain per unit are compared to A and B alloys. However, the results

suggest that the beneficial effect of Cr may have an upper limit beyond which the gain in oxidation resistance is not much. In fact, the alloys tend to be very brittle with high Cr concentrations.

10. PRODUCTS

Conference Presentations:

1. “High Temperature Oxidation of a Nb-W-Cr Alloy in Air Up To 1400°C”, Purushotham R. Kakarlapudi, Shailendra Varma, and Ken Natesan, Fifteenth International Symposium on Processing and Fabrication of Advanced Materials (PFAM XV), Materials Science & Technology 2006, Cincinnati, Ohio, October 16, 2006.
2. Oxidation of Nb Based Alloys Between 700 and 1400°C”, Shailendra Varma, Purushotham R. Kakarlapudi, Abdul Bhuiya, and Ken Natesan, 210th Electrochemical Society Meeting, High Temperature Corrosion and Materials Chemistry, Cancun, Mexico, October 30, 2006.
3. “Alloys from Nb-W-Cr System for High Temperature Applications”, Purushotham R. Kakarlapudi, Shailendra Varma, and Ken Natesan, TMS 2007, 136th Annual Meeting Refractory Metals 2007: Oxidation and Thin Films, Orlando, Florida, February 26, 2007.
4. “Characterization of Oxidation Products in Ternary Alloys Containing C Modifiers”, Maria D. Gonzalez, Purushotham Kakarlapudi, Benedict Portillo, and S.K. Varma, Materials Science and Technology 2007, Fundamentals and Characterization: High Temperature Material Systems, Detroit, Michigan, September 20, 2007.
5. “Effect of Boron on High Temperature Oxidation Resistance of Alloys from Nb-W-Cr System”, Benedict Portillo, Purushotham Kakarlapudi, and S.K. Varma, Materials Science and Technology 2007, Fundamentals and Characterization: High Temperature Material Systems, Detroit, Michigan, September 20, 2007.
6. Oxidation Behavior of Alloys from Nb-W-Cr System Containing C Modifiers, Maria D. Gonzalez and S.K. Varma, TMS 2008, 137th Annual Meeting and Exhibition, Refractory Metals 2008: Properties of Refractory Metals, New Orleans, Louisiana, March 13, 2008.

Publications:

1. “High Temperature Oxidation of Nb-20W-10Cr Alloy in Air at up to 1400°C”, Purushotham Kakarlapudi, Shailendra Varma, and Ken Natesan, Proceedings of Fifteenth International Symposium on Processing and Fabrication of advanced

Materials (PFAM XV), Editors: R. Varin and T.S. Srivatsan, Materials Science and Technology (MS&T) 2006, ASM, Warrendale, PA, pp. 131-139, 2006.

2. "Exploration of Nb-W-Cr Alloys for High Temperature Applications in Air", Benedict Portillo, Purushotham Kakarlapudi, and S.K. Varma, Journal of Metals, pp. 46-50, June 2007.
3. "Oxidation Behavior of Alloys from the Nb-W-Cr System Containing C Modifiers", Maria D. Gonzalez and S.K. Varma, TMS 2008 Proceedings, Vol I: Materials Processing and Properties, 2008, pp.455-460.
4. "High Temperature Oxidation Characteristics of Alloys from the Nb-W-Cr System with C Additions", Maria D. Moricca and S.K. Varma, Journal of Metals, Refractory Metals issue, Vol 60 (7) (2008) pp. 66-69.
5. "Oxidation Resistant NbCr₂ Phase in Nb-W-Cr System", Julieta Ventura, Benedict Portillo, and S.K. Varma, Journal of Alloys and Compounds, in press (JALCOM-18549).

Theses and Dissertations:

1. "High Temperature Oxidation Response of Nb-20W-10Cr in Air". Purushotham R. Kakarlapudi, The M.S. thesis was successfully defended on May 14, 2007 in the Department of Metallurgical and Materials Engineering, The University of Texas at El Paso.
2. "High Temperature Oxidation Behavior of the Nb-W-Cr System and Response to Boron Additions". Benedict I. Portillo, The M.S. thesis was successfully defended on May 14, 2008 in the Department of Metallurgical and Materials Engineering, the University of Texas at El Paso.
3. "Effect of Cr on the Oxidation Resistant of Alloys from Nb-W-Cr System" Maria D. Moricca, Ph.D. Dissertation, Expected in Spring Semester 2009.