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THEORETICAL ANALYSIS OF COMPATIBILITY OF SEVERAL REINFORCEMENT MATERIALS WITH NiAl AND FeAl MATRICES

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ABSTRACT

Several potential reinforcement materials were assessed for their chemical, coefficient of thermal expansion (CTE), and mechanical compatibility with the intermetallic matrices based on NiAl and FeAl. Among the ceramic reinforcement materials, Al_2O_3, TiC, and TiB_2, appear to be the optimum choices for NiAl and FeAl matrices. However, the problem of CTE mismatch with the matrix needs to be solved for these three reinforcement materials. Beryllium-rich intermetallic compounds can be considered as potential reinforcement materials provided suitable reaction barrier coatings can be developed for these. Based on preliminary thermodynamic calculations, Sc_2O_3 and TiC appear to be suitable as reaction barrier coatings for the beryllides. Several reaction barrier coatings are also suggested for the currently available SiC fibers.

INTRODUCTION

Iron and nickel aluminides are currently being considered as potential high temperature structural materials. The Ni-Al alloys of interest as high temperature materials are within the β' NiAl phase with compositions ranging from 40 to 50 a/o Al. These alloys are expected to be used in the temperature range 1373 - 1573 K. The Fe-Al alloys of interest are the α_2 phase FeAl alloys with compositions ranging from 40 to 50 a/o Al. The upper use temperature for FeAl alloys will be in the range of 1173 - 1273 K.

There are two prime reasons for the current interest in FeAl and NiAl alloys for high temperature structural applications. First, these two aluminides have excellent oxidation resistance at high temperatures. Second, there is some hope of attaining room temperature ductility for these two aluminide systems. The FeAl alloy with 40 a/o Al has exhibited room temperature ductility, in the range of 3 to 5 percent elongation (ref. 1). Significant (about 2 - 2.5 %) ductility has also been reported (refs. 2 and 3) for the stoichiometric NiAl at room temperature. One potential drawback for NiAl and FeAl alloys is their loss of strength at higher temperatures. This can be overcome by reinforcing the aluminide matrices with high strenth, high modulus fibers. These fibers will, then, carry the major portion of the load.

The requirements for an ideal reinforcement material for the aluminide matrices are: (1) high modulus, (2) high strength at elevated temperatures, (3) chemical compatibility with the matrix, and (4) close match in coefficient of thermal expansion (CTE) with that of the matrix. The long-term stability of the composite is dictated by the last two criteria described above, i.e, chemical compatibility and CTE compatibility. Therefore these two factors are expected to be important in selecting a reinforcement material for a given matrix.

For high temperature applications, SiC fibers, processed either via chemical vapor deposition or from polymer precursors, are the only ones commercially available at this time. Unfortunately, thermodynamic calculations (refs. 4 and 5) and limited experimental studies (refs. 6 and 7) have shown that SiC is not chemically compatible with NiAl and FeAl matrices. This necessitates the development of suitable reaction barrier coatings for the SiC fibers. Furthermore, the CTE for SiC is considerably lower than that of NiAl and FeAl alloys. Thus there is a great need for identification of alternate fiber compositions, and this is one of the main objectives of this work.

In this study the chemically compatible reinforcement materials are identified based on thermodynamic considerations, and then these chemically compatible reinforcement materials are assessed for their CTE and mechanical compatibility with the matrix. In order to identify potential reinforcement materials, one can first screen different candidate materials for CTE and mechanical compatibility with the matrices and then assess the chemical compatibility for those compositions which look promising in terms of CTE and mechanical compatibility. However, identifying chemically compatible compositions first, as is done in this study, offers one distinct advantage -- that is to provide guidelines for selecting coating compositions for the fibers.

It is probably almost impossible for one candidate fiber material to satisfy all the criteria described above. If a fiber has high modulus and good strength properties, but is not chemically compatible with the matrix, then suitable coatings can be applied to the fiber which will serve as a reaction barrier. Thus the second objective of this study is to identify coating compositions for reinforcement materials that have good CTE and mechanical compatibility with the matrix, but are not chemically compatible with the matrix. Also, suitable reaction barrier coatings will be identified for the currently available SiC fibers. The identification of coating compositions for the reinforcement materials are based on thermodynamic analysis of the reinforcement material-coating and coating-matrix interactions.

REINFORCEMENT MATERIALS CONSIDERED IN THIS STUDY

The reinforcement materials considered in this study include carbides, borides, nitrides, oxides, beryllides, and silicides and are given in Table I. The reinforcement materials were chosen primarily because of their high melting points.

TABLE I
Reinforcement Materials Considered in This Study

Carbides	Borides	Oxides	Nitrides	Berrylides	Silicides
B_4C	AlB_{12}	Al_2O_3	AlN	$Be_{13}La$	Cr_3Si
HfC	CrB_2	BeO	BN	$Be_{13}Y$	Cr_5Si_3
Mo_2C	HfB_2	CaO	HfN	$Be_{13}Zr$	Mo_3Si
Nb_2C	LaB_6	CeO_2	LaN	$Be_{17}Nb_2$	Mo_5Si_3
NbC	NbB_2	Cr_2O_3	Si_3N_4	$Be_{17}Ti_2$	$MoSi_2$
SiC	ScB_2	Gd_2O_3	TaN	$Be_{17}Ta_2$	Nb_5Si_3
TaC	TaB_2	HfO_2	TiN		$NbSi_2$
Ta_2C	TiB_2	La_2O_3	ZrN		Ta_2Si
TiC	TiB	MgO			Ta_5Si_3
V_2C	VB	Sc_2O_3			$TaSi_2$
VC	VB_2	SiO_2			Ti_5Si_3
W_2C	V_3B_2	TiO			$TiSi$
WC	V_2B_3	TiO_2			V_3Si
ZrC	ZrB_2	Y_2O_3			V_5Si_3
		ZrO_2			VSi_2
		Ca_2SiO_4			W_5Si_3
		$CaZrO_3$			WSi_2
		$Y_2O_3.2ZrO_2$			Zr_2Si
					Zr_5Si_3
					$ZrSi$

THERMODYNAMIC ANALYSIS OF CHEMICAL INTERACTIONS BETWEEN ALUMINIDE MATRICES AND REINFORCEMENT MATERIALS

The details of thermodynamic analysis of chemical interactions between the reinforcement materials and intermetallic matrices have been described elsewhere (refs. 4 and 5) and, therefore, only a brief summary will be given here. The sequence of steps involved in determining the chemical compatibility of a reinforcement material CD in an intermetallic matrix AB are given in Fig. 1. Primarily, three different modes of reaction are considered in determining the chemical stability of a reinforcement material in an intermetallic matrix. These are briefly described below.

(1) Direct reduction of the reinforcement material by an element of the intermetallic matrix: An example of this type of reaction is the reduction of B_4C by the Fe component of FeAl alloys to form FeB and carbon at unit activity via:

$$4\underline{Fe} + B_4C = 4FeB + C \qquad [1]$$

The underline in the above reaction denotes that the element is present at a reduced activity in the alloy. Reaction of NiAl alloys with SiC also occurs by a similar reaction which is written as:

$$2\underline{Ni} + SiC = Ni_2Si + C \qquad [2]$$

(2) Simultaneous formation of two product compounds: Two compounds can be formed simultaneously by reaction of the reinforcement material with either one component or both the components of the intermetallic matrix. Examples of this type of reaction are:

$$10\underline{Al} + 3CeO_2 = 2Al_2O_3 + 3Al_2Ce \qquad [3]$$

$$6\underline{Fe} + 4\underline{Al} + 3ZrO_2 = 2Al_2O_3 + 3Fe_2Zr \qquad [4]$$

In reaction [3], only one component of the intermetallic matrix reacts with the reinforcement phase, whereas, in reaction [4] both the components of the intermetallic matrix react simultaneously with the reinforcement phase.

(3) Dissolution of the elements of the reinforcement material in the matrix: As an example, consider reaction of TiB_2 with NiAl alloys. Thermodynamic calculations show that reaction modes [1] and [2] are not feasible for NiAl-TiB_2 system. However, dissolution of Ti and B in the intermetallic matrix would occur. The minimum value for the activity of Ti in the matrix can be calculated from the equilibria for the reaction:

$$\underline{Al} + 6TiB_2 = AlB_{12} + 6\underline{Ti} \qquad [5]$$

Similarly, the minimum value for the activity of B in the matrix can be calculated from the equilibria for the reaction:

$$3\underline{Ni} + TiB_2 = Ni_3Ti + 2\underline{B} \qquad [6]$$

In our calculations, if the calculated minimum values for the activities of Ti and B in the matrix are less than 10^{-3}, then the reinforcement material can be considered to be chemically compatible with the matrix.

CHEMICALLY COMPATIBLE REINFORCEMENT MATERIALS

(a) NiAl matrices: Since the NiAl-based composite systems are expected to be used in the temperature range 1373 - 1573 K, all the thermodynamic calculations for NiAl matrices were made at two temperatures, i.e., 1573 and 1373 K. A list of chemically compatible reinforcement materials for NiAl matrices at these two temperatures are given in Table II. Note that CaO and ZrO_2 are not compatible with all NiAl compositions in the range 40 - 50 a/o Al. The compound CaO would be compatible with NiAl alloys for Al concentrations less than or equal to 49 a/o. At the equiatomic NiAl composition, thermodynamic calculations show that $CaAl_2O_4$ and $CaAl_2$ are likely to be formed as a result of reaction of the Al component of the alloy with CaO. It is likely that the reaction between CaO and Ni50Al alloy will be of only limited extent since any reaction of the Al component of the alloy would decrease the Al concentration at the interface. Similary, the compound ZrO_2 is not compatible with NiAl alloys with Al concentrations lower than 42 a/o because of simultaneous formation of Ni_7Zr_2 and Al_2O_3. However, this may not be of any concern since potential NiAl alloys are likely to be of compositions closer to the equiatomic composition.

TABLE II

Chemically compatible reinforcement materials for NiAl alloys

HfC	ScB_2	CaO^1	MgO^2	$CaZrO_3$	TiN
TiC	TiB_2	Gd_2O_3	Sc_2O_3	$Y_2O_3.2ZrO_2$	ZrN
ZrC	Al_2O_3	HfO_2	Y_2O_3	AlN	Mo_3Si
HfB_2	BeO	La_2O_3	ZrO_2	HfN	Mo_5Si

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1. Compatible for compositions lower than or equal to 49 a/o Al.
2. Compatible if MgO is completely embeded in the matrix.

The compound MgO would be compatible with NiAl alloys provided the reinforcement material is completely embeded in the matrix. This is because of formation of Mg(g) by the reaction:

$$2\underline{Al} + 3MgO = Al_2O_3 + 3Mg(g) \qquad [7]$$

The equilibrium p_{Mg} at 1573 and 1373 K for the above reaction for NiAl is calculated to be 0.038 atm, and $3.55*10^{-3}$ atm, respectively, which are quite high. Thus if the reinforcement material-matrix inteface is exposed to a dynamic environment, gaseous Mg will be continuously swept away by the high velocity gases resulting in conversion of MgO to Al_2O_3.

Besides the reinforcement materials listed in Table II, there are probably few other materials which might be compatible with NiAl matrices provided dissolution of small amounts of the elements of the reinforcement material in the matrix can be tolerated. One such example is CrB_2. Thermodynamic calculations show that the minimum value for the activities of Cr and B in the equiatomic NiAl alloy would be on the order of $1.98*10^{-3}$ and 0.017, respectively at 1573 K. It is likely that the solubility of B in NiAl is negligible. Thus only a small amount of Cr, possibly on the order of 0.1 %, would be dissoved in NiAl at 1573 K. This level of Cr can probably be tolerated in the matrix. The minimum value for the equilibrium activity of Cr is even lower ($7.13*10^{-4}$) at 1373 K. Thus CrB_2 would be compatible with NiAl at 1373 K.

<u>(2) FeAl matrices:</u> All the thermodynamic calculations for FeAl matrices were undertaken at 1273 K. Table III gives a list of chemically reinforcement materials at this temperature. Note that CrB_2, although marginally compatible with NiAl, is not compatible with FeAl alloys. The minimum equilibrium activity of Cr in the matrix for FeAl-CrB_2 combination at 1273 K is calculated to be 0.33, which is too high. Thus large amount of Cr is expected to be dissolved in the matrix.

TABLE III

Chemically compatible reinforcement materials for FeAl matrices

HfC
TiC
ZrC
HfB_2
ScB_2
ZrB_2
TiB_2
Al_2O_3
BeO
Gd_2O_3
La_2O_3
MgO[1]
Sc_2O_3
Y_2O_3
AlN
HfN
Ti_5Si_3

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1. Compatible if MgO is completely embeded in the matrix.

IDENTIFICATION OF POTENTIAL REINFORCEMENT MATERIALS

Besides chemical compatibility, other properties like coefficients of thermal expansion, elastic modulus, and high temperature strength are important in selecting a reinforcement material for a given matrix. Strength of ceramic materials in fiber form are generally not known and, therefore, this will not be considered in selecting a reinforcement material composition. However, in general, a material with high elastic modulus is expected to have high strength.

The linear thermal expansions as a function of temperature for the chemically compatible reinforcement materials (from Tables II and III) are shown in Fig. 2. Also shown in Fig. 2 are the linear thermal expansions for NiAl and FeAl. Thermal expansion data for all the compounds except for fully stabilized (cubic) ZrO_2 and CrB_2 were taken from the compilations by Touloukian (refs. 8 and 9). The thermal expansion data for fully stabilized ZrO_2 were taken from the review paper by Garvie (ref. 10). The expansion data for CrB_2 were taken from the work of Lonnberg (ref. 11). The thermal expansion versus temperature behavior for Gd_2O_3, Sc_2O_3, and Y_2O_3 are nearly the same as that of Al_2O_3 and, therefore, are not shown in Fig. 2 in order to maintain clarity.

The elastic modulus for the chemically compatible materials are listed in Table IV. Also shown in Table IV are the elastic modulus for NiAl and FeAl. The elastic modulus for all the ceramic materials except for CrB_2 were taken form refs. 12 - 15. The elastic modulus data for CrB_2 was taen from the review paper by Fleischer (ref. 16). The modulus data for NiAl and FeAl were taken from the work of Harmouche and Wolfenden (refs. 17 and 18).

The chemically compatible reinforcement materials for NiAl matrices are listed in Table V in order of increasing CTE mismatch with the aluminide matrices. A number of reinforcement materials on the same line indicate that they have nearly the same coefficients for thermal expansion. The CTE data for a few chemically compatible reinforcement materials are not available and therefore are not shown in Table V. The same order as shown in Table V is also valid for FeAl alloys; however, a few of the reinforcement materials listed in this table like CaO, $CaZrO_3$, Cubic ZrO_2, CrB_2, TiN, and ZrN are not chemically compatible with FeAl alloys.

TABLE IV

Elastic modulus (E) for different materials

Compound	E in GPa (Room Tempr.)	E in GPa (Higher Tempr.)
Al_2O_3(single crystal)	474	440 (1400 K)
Al_2O_3(polycrystalline)	443	415 (1373 K)
BeO	385	352 (1373 K) 324 (1473 K)
CaO	-	-
$CaZrO_3$	-	-
Gd_2O_3	135	121 (1366 K)
HfO_2	-	-
La_2O_3	-	-
MgO	372-387	323 (1373 K)
Sc_2O_3	220	189 (1366 K)
Y_2O_3	148 - 169	135 (1366 K)
ZrO_2	237 - 253	162 (1200 K) 148 (1373 K)
$ZrO_2(Y_2O_3)$	304	162 (1000 K)
ZrO_2(MgO)	210	169 (1300 K)
ZrO_2(CaO)	149	101 (1300 K)
HfC	324	284 (1366 K)
TiC	448 - 480	433 (1366 K)
ZrC	385	365 (1373 K)
SiC(CVD)	412	365 (1213 K) 331 (1477 K)
SiC(Hot press)	426	372 (1644 K)
AlN	345	310 (1373 K)
TiN	245 - 600$^{?}$	-
ZrN	-	-
CrB_2	~212	-
TiB_2	496	-
ZrB_2	496	-
NiAl	237	180 (1273 K)
Ni40a/o Al	231	172 (1273 K)
FeAl	256	-
Fe40a/oAl	252	-

Table V

Chemically compatible reinforcement materials for NiAl matrices in order of increasing CTE mismatch with the matrix

Increasing CTE mismatch ↓

MgO
CaO, La_2O_3
$CaZrO_3$, CrB_2
Fully stabilized ZrO_2(cubic)
BeO, TiN
Al_2O_3, Sc_2O_3, Y_2O_3, Gd_2O_3
TiC, TiB_2, ZrN
HfB_2, ZrB_2, HfC, ZrC
AlN

Potential reinforcement materials for NiAl alloys: The thermal expansion behavior for three chemically compatible ceramic materials match closely with that of NiAl. These are La_2O_3, CaO, and MgO. The oxide MgO has a high elastic modulus both at room temperature and at elevated temperature, and can possibly be a good fiber material for NiAl matrices. However, MgO has a tendency to hydrate in contact with moisture and this may pose serious problems. Furthermore, as discussed earlier, reaction of MgO with NiAl alloys leads to formation of Al_2O_3 and Mg(g) and, if the interface is exposed to a dynamic environment, the reaction is likely to proceed continuously as Mg(g) is removed from the interface. However, once a layer of Al_2O_3 or $MgAl_2O_4$ is formed, it is likely that the reaction will stop. Possibly, a coating of $MgAl_2O_4$ can be applied on MgO to prevent the reaction between MgO and NiAl alloys. There are no data on the elastic modulus of CaO and La_2O_3. The elastic modulus for La_2O_3 is probably low since the modulus for the oxides of other elements in the same group as La in the periodic table, i.e, Sc_2O_3, and Y_2O_3, are low. The elastic modulus for these oxides is even lower than that of NiAl. Thus La_2O_3 may not be suitable as a reinforcement material for NiAl.

The compounds $CaZrO_3$, fully stabilized ZrO_2, and CrB_2 have coefficients of thermal expansion lower than that of CaO, MgO, and La_2O_3; however, the CTE for these three compounds are still higher than other chemically compatible reinforcement materials. The elastic modulus of yttria stabilized ZrO_2 is slightly higher than that for NiAl at room temperature, but lower than that of NiAl at higher temperatures. The elastic modulus for MgO and CaO stabilized ZrO_2 are lower than that for NiAl even at room temperature. There are no data on the elastic modulus for $CaZrO_3$. Based on the fact that the elastic modulus of calcia stabilized ZrO_2 is quite low, it is expected that the elastic modulus for $CaZrO_3$ would also be low. Thus stabilized ZrO_2 and $CaZrO_3$ are not likely to be suitable as reinforcement materials for NiAl matrices. The elastic modulus for CrB_2 appears to be lower than that for NiAl alloys at room temperature and therefore may not be suitable as a reinforcement material for NiAl matrices.

There are several other oxides which have slightly lower CTE values than that of stabilized ZrO_2. These are BeO, Al_2O_3, Sc_2O_3, Y_2O_3, and Gd_2O_3. Among these the rare earth oxides like Sc_2O_3, Y_2O_3, and Gd_2O_3 have low elastic modulus (much lower than NiAl) and, therefore, are not suitable as reinforcement materials. On the other hand, oxides like Al_2O_3 and BeO have high modulus and can be considered as potential reinforcement materials. Among the carbides, TiC has the highest coefficient of expansion, its coefficient being slightly lower than that of Al_2O_3. In addition, the elastic modulus of TiC is quite high. The expansion behavior for TiB_2 is similar to that of TiC. Also, the elastic modulus for TiB_2 is quite high. Among nitrides, TiN has the highest CTE value, its expansion coefficient being slightly greater than that of Al_2O_3. There are large disecrepancies in the literature on the elastic modulus of TiN ranging from 245 to 600 GPa at room temperature.

Based on the above discussions it becomes clear that none of the materials that are both chemically compatible and CTE compatible have adequate mechanical properties to be considered as potential reinforcement materials. Thus one must chose reinforcement materials that have lower expansion coefficients than that of NiAl. Possible candidate materials are BeO, Al_2O_3, TiC, TiB_2, and TiN. An oxide fiber is definitely preferable because of oxidation problems associated with non oxides. Among the oxides Al_2O_3 is to be preferred over BeO because of three factors: (1) Al_2O_3 has a higher modulus compared to that of BeO, (2) BeO is toxic in powder form, and (3) BeO does not offer significant advantages over Al_2O_3 in terms of CTE.

Use of low CTE fibers such as Al_2O_3, TiC, or TiB_2 requires that suitable design methodologies be developed to circumvent the problem of CTE mismatch between the fiber and the matrix. One approach would be to introduce a ductile interlayer between the fiber and the matrix. The effectiveness of a ductile interlayer in reducing the thermal stresses has already been demonstrated for metal-ceramic joining (ref 19). Another concept that had some success in the field of metal-ceramic joining is to introduce a cermet layer consisting of ceramic dispersions in a metal matrix (ref. 20). A possible cermet layer for NiAl/Al_2O_3 composite would be Al_2O_3 dispersed in NiAl.

Potential reinforcement materials for FeAl alloys: The same considerations as discussed above for NiAl alloys would apply to FeAl alloys. The possible reinforcement materials for FeAl matrix would be Al_2O_3, TiC, and TiB_2. The extent of CTE mismatch between these fibers and FeAl alloys would be greater than that for NiAl alloys because of higher CTE for iron aluminides.

Beryllides as potential reinforcement materials: Beryllium-rich intermetallic compounds such as $Be_{17}Nb_2$, $Be_{17}Ta_2$, and other similar compositions have many interesting properties. Figure 3 compares the thermal expansion behavior for a few beryllides with NiAl and FeAl. All the Be-rich intermetallic compounds have coefficients of thermal expansion similar to that of NiAl. Also, there is reasonable match in CTE between the beryllides and FeAl alloys. Limited elastic modulus data (ref. 21) for two of the beryllides, shown in Table VI, indicate high modulus values for the

TABLE VI

Elastic modulus (E) for Ta and Nb beryllides

Compound	E, GPa (Room tempr)	E, GPa (High Tempr)	Testing method
Ta_2Be_{17}	372	216 (1366 K)	Static test
	189	216 (1366 K)	Dynamic test
Nb_2Be_{17}	304	196 (1366 K)	Static test
	284	331 (1366 K)	Dynamic test

beryllides. Based on higher melting points, high modulus values, and close match in CTE between the beryllides and aluminides, it becomes apparent that Be-rich intermetallic compounds would be ideal candidate reinforcement materials for NiAl and FeAl matrices. However there is one major drawback for beryllides as reinforcement materials. That is, the beryllides would react with both NiAl and FeAl matrices. Reaction of NiAl alloys with Be-rich compounds would lead to the formation of NiBe. Similarly, the intermetallic compound $FeBe_2$ is likely to be formed by the reaction of FeAl alloys with Be-rich intermetallic compounds.

Succesful use of beryllides as reinforcements requires that coatings which will act as reaction barriers must be developed. The attractive mechanical and thermal expansion properties of the beryllides provide incentives for development of such reaction barrier coatings.

REACTION BARRIER COATINGS FOR REINFORCEMENT MATERIALS

In many cases where a reinforcement material has many desirable properties but reacts with the matrices, suitable reaction barrier coatings must be developed. A convenient way of identifying reaction barrier coatings for a given reinforcement - matrix combination is to analyze reinforcement-coating and coating-matrix interactions from thermodynamic considerations. In this section thermodynamic principles will be applied to identify reaction barrier coatings for two reinforcement materials: (1) SiC, and (2) Be-rich intermetallic compounds.

Reaction barrier coatings for SiC fibers

Ceramic materials that are compatible with NiAl and FeAl matrices have already been identified and were shown in Tables II and III. Carbide coatings are not feasible for SiC fibers because of formation of compounds or solid solutions betweem SiC and other carbides. Since many of the oxides and borides are chemically compatible with both NiAl and FeAl matrices, these become prime candidates for coatings on SiC fibers.

(a) Reaction of oxides with SiC: The reaction of several oxides with SiC were analyzed by means of the multi-component equilibrium program "SOLGAS", originally developed by Eriksson et. al. (ref. 22) and later modified by Bessman (ref. 23). The possible oxide coatings considered are Al_2O_3, BeO, CaO, MgO, La_2O_3, Y_2O_3, Sc_2O_3, Gd_2O_3, and ZrO_2. The major reaction products between SiC and the oxides, except for ZrO_2, can be written as:

$$ySiC + 2M_xO_y = ySiO(g) + yCO(g) + 2xM(g) \qquad [8]$$

Ex: $$3SiC + 2Al_2O_3 = 3SiO(g) + 3CO(g) + 4Al(g) \qquad [9]$$

The reaction between SiC and ZrO_2 can be written as:

$$6SiC + 4ZrO_2 = 2ZrC + 2ZrSi + 4SiO(g) + 4CO(g) \qquad [10]$$

As seen from reactions [8] - [10], gaseous reaction products are likely to be formed as a result of reaction of SiC with the oxides. The total pressure of gaseous reaction products at the fiber-coating interface determines the extent of reaction between the fiber and the coating. Table VII gives the total pressure at the fiber-coating interface at 1573 K for various SiC-oxide combinations.

If there are no paths for product gases to escape from the fiber-coating interface, the reaction between the SiC fiber and the oxide coating will stop once the total pressure of gaseous products at the fiber-coating interface reaches their equilibrium values. In such cases all the oxides shown in Table VII are likely to be compatible with the SiC fiber. However, if there are cracks or high diffusion paths at the fiber-coating interface through which the gases can escape, the reaction between the fiber and the oxide coating will proceed continuously. Then, the oxides towards the top of the list in Table VII, i.e., oxides for which the equilibrium total pressures at the SiC-oxide interface are calculated to be low, are likely to be compatible with SiC. The oxides Y_2O_3, La_2O_3, Gd_2O_3, and Sc_2O_3 appear to be the best coating compositions in such situations.

TABLE VII

Equilibrium total pressure of gaseous reaction products developed at SiC-oxide interface at 1573 K

Oxide	-Log(Pressure), atm.	
Y_2O_3	7.78	↑ Increasing chemical compatibility
La_2O_3	7.35	
Gd_2O_3	7.03	
Sc_2O_3	7.01	
BeO	5.72	
Al_2O_3	4.74	
CaO	4.07	
ZrO_2	3.58	
MgO	2.78	

The commercially available SiC fibers such as SCS-6 have a carbon-rich layer on the surface. Then, the reaction between this carbon layer and the oxide coatings needs to be considered. Equilibrium calculations show that reaction between the oxides and carbon would lead to formation of carbide along with gaseous species such as CO(g) and Me(g) where Me is the metallic element of the oxide. Examples of this type of reaction are:

$$3Al_2O_3 + 9C = Al_4C_3 + 2Al(g) + 9CO(g) \qquad [11]$$

$$2CaO + 4C = CaC_2 + Ca(g) + 2CO(g) \qquad [12]$$

The zirconium gas is not likely to be formed as a result of reaction of ZrO_2 with carbon. Instead, only ZrC and CO(g) are likely to be formed by the reaction

$$ZrO_2 + 3C = ZrC + 2CO(g) \qquad [13]$$

Similar to that of SiC-oxide reaction, the magnitude of equilibrium total pressure of product gases at oxide-carbon interface determines the extent of reaction between the oxide and carbon. Table VIII gives the equilibrium total pressures for various oxide-carbon combinations at 1573 K. There are no thermodynamic data for the carbides of Gd, Sc, and Y. Therefore the equilibrium total pressures for the reaction of these oxides with carbon are not shown in Table VIII. Note that the equilibrium total pressures at the oxide-carbon interface are higher than that at the oxide-carbide interface. However, unlike that of the oxide-SiC interface (except for ZrO_2-SiC interface), a solid reaction product, i.e, carbide, is formed by reaction of oxides with carbon. Once a layer of solid carbide is formed at the oxide-carbon interface, further reaction will probably stop because of inability of product gases to escape through a solid carbide layer.

TABLE VIII

Equilibrium total pressure of gaseous products developed at oxide-carbon interface at 1573 K

Oxide	-Log(pressure), atm.
La_2O_3	5.7
BeO	5.22
MgO	4.17
Al_2O_3	3.83
CaO	3.6
ZrO_2	2.0

↑ Increasing compatibility

In summary, many of the rare earth oxides like La_2O_3, Gd_2O_3, and Sc_2O_3 appear to be ideal coating compositions for SiC fibers. Al_2O_3 coatings would also be suitable provided there are no fast diffusion paths for the reaction product gases to escape to the atmosphere.

(b) Reaction of SiC with TiB_2: The compound TiB_2 can exist over a narrow composition range from 65.5 to 67 at. % B (ref. 24). The activity of Ti and B can vary by large orders of magnitude over this narrow composition range (ref. 20). Thermodynamic calculations show that reaction of SiC with TiB_2 at the Ti-rich boundary would lead to formation of TiC and Ti_5Si_3. At the Ti-rich boundary, the activity of B is low and, therefore, no reaction is expected between the B component of TiB_2 and SiC at the Ti-rich boundary. On the other hand, at the B-rich boundary of TiB_2, the boron component of TiB_2 would react with SiC to form B_4C and free Si. No reaction between the Ti component of TiB_2 and SiC is expected at this boundary.

Calculations show that no reaction is to be expected between stoichiometric TiB_2 and SiC. Since only one component of TiB_2 is likely to react with SiC at either end of the TiB_2 boundary, the composition of TiB_2 would move towards the stoichiometric composition after the initial reaction, and the reaction will stop.

Reaction of Ti-rich TiB_2 with carbon coating on SiC would lead to formation of TiC, wheras reaction with B-rich TiB_2 would lead to formation of B_4C. No reaction is to be expected between stoichiometric TiB_2 and carbon.

In summary, stoichiometric TiB_2 is chemically compatible with both SiC and carbon. Any reaction between nonstoichiometric TiB_2 and SiC or C would be minor.

Reaction barrier coatings for beryllides

The activity of Be in the Be-rich intermetallic compounds like $Be_{17}Ta_2$ is very high, being on the order of 0.3 or higher (ref. 25). Because of the high stability of BeO, the Be component of beryllides is likely to reduce many oxides which are thermodynamically less stable than BeO. Two oxides can possibly be compatible with the beryllides. These are: Gd_2O_3 and Sc_2O_3. Reaction of Be component of the beryllides with these two oxides can be written as:

$$3\underline{Be} + Gd_2O_3 = 3BeO + 2\underline{Gd} \qquad [14]$$

$$3\underline{Be} + Sc_2O_3 = 3BeO + 2\underline{Sc} \qquad [15]$$

The equilibrium activity of Gd and Sc, assuming the activity of Be to be 0.3, are 0.158 and $8.355*10^{-3}$, respectively. The equilibrium activity of Gd for reaction [14] is very high. Thus Gd_2O_3 would be compatible with the beryllides provided Gd is not soluble in the beryllides. Since the equilibrium activity of Sc for reaction [15] is comparatively low, Sc_2O_3 is likely to be compatible with the beryllides.

Among the carbides, TiC is a likely coating material for the beryllides. The equilibrium Ti activity for the reaction

$$2\underline{Be} + TiC = Be_2C + \underline{Ti} \qquad [16]$$

is $3.02*10^{-3}$, which is reasonably low.

No boride coatings for beryllides were analyzed in this study because of the lack of thermodynamic data for Be-B compounds. Besides the ceramic coatings for beryllides, other high melting intermetallic compounds like the Engel-Brewer compouds might also be suitable as coating compositions for the beryllides. These too were not considered in this study because of lack of thermodynamic data for many relevant compounds.

SUMMARY AND CONCLUDING REMARKS

After examination of the chemical compatibility, the thermal expansion behavior, and the elastic modulus of several ceramic materials, it becomes apparent that none of the ceramic materials have all the desired properties to be considered as reinforcement materials for NiAl and FeAl matrices. The ceramic materials that are chemically compatible and have a reasonably close match in CTE with the aluminides suffer from one drawback. That is, they have low elastic modulus. Since the elastic modulus is an inherent property of a material, very little can be done to change this. Furthermore, the materials having low elastic modulus are also expected to have low strength. Thus one must settle for ceramic materials with lower CTE, but with superior mechanical and chemical properties. Three ceramic materials are recommended for NiAl and FeAl alloys. These are Al_2O_3, TiC, and TiB_2. Alumina is to be preferred over TiC and TiB_2 because of oxidation problems associated with the later two materials. However, serious research efforts must be directed towards solving the problem of CTE mismatch between the fiber and the matrix, possibly by using a compliant layer between the fiber and the matrix. Also, the bonding between the fibers and the matrix needs to be optimized.

Beryllides offer some potential as reinforcement materials for NiAl and FeAl matrices because of their high CTE and reasonably good mechanical properties. However, they are likely to react with the NiAl and FeAl matrices. Therefore suitable reaction barrier coatings must be developed. Two coating compositions, Sc_2O_3 and TiC, are suggested based on preliminary thermodynamic analysis.

Several reaction barrier coatings such as La_2O_3, Gd_2O_3, Sc_2O_3, Al_2O_3, and TiB_2 have been suggested in this study for the SiC fibers. However, the extent of CTE mismatch with the matrix is much greater for the SiC fibers as compared to other fiber compositions like Al_2O_3, TiC, and TiB_2. Thus, even though a reaction barrier coating can be applied on SiC fibers, the problem of CTE mismatch still needs to be addressed.

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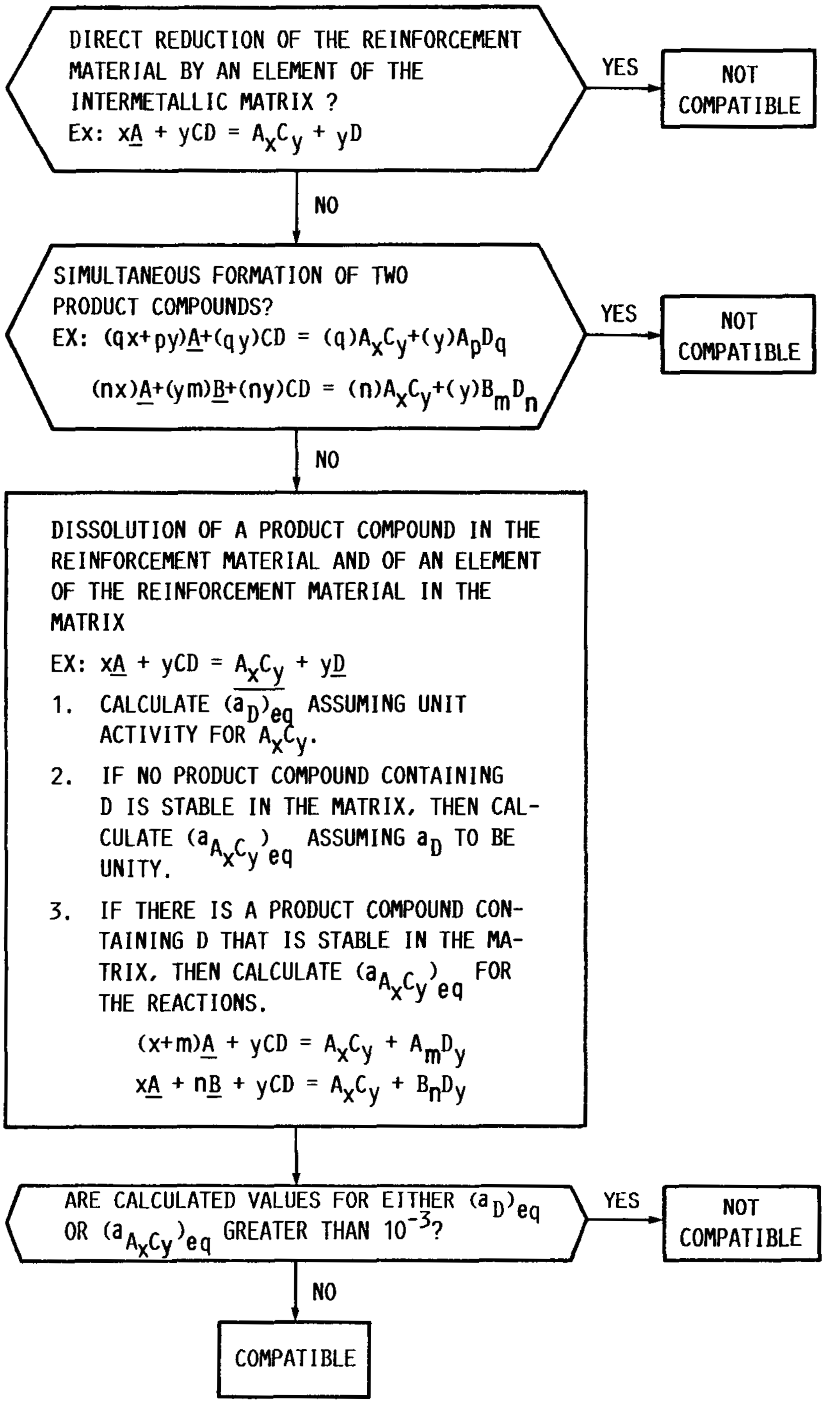

FIGURE 1. - SEQUENCE OF STEPS IN CALCULATING THE CHEMICAL COMPATIBILITY OF A REINFORCEMENT MATERIAL CD WITH AN INTERMETALLIC MATRIX AB.

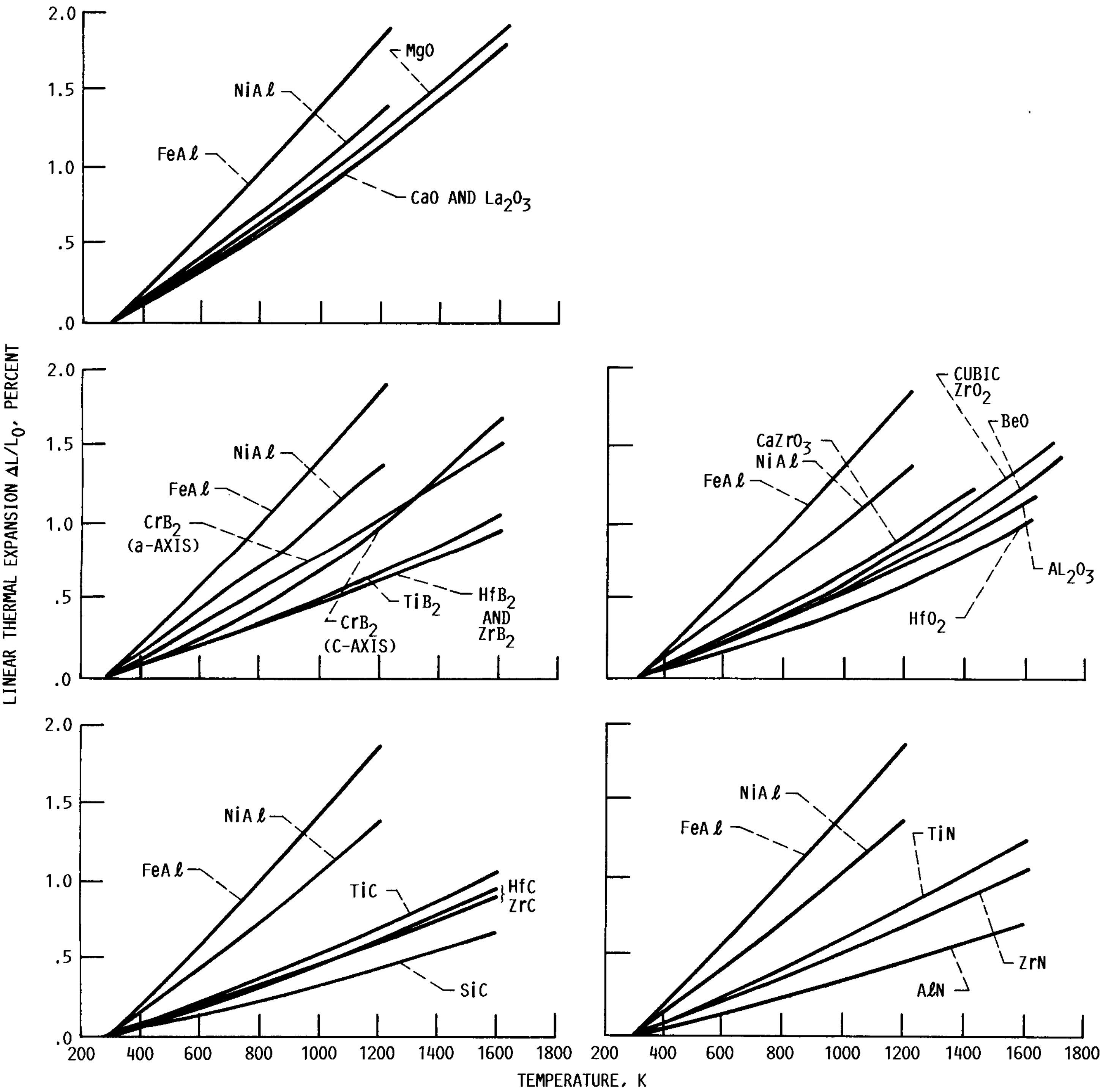

FIGURE 2. - COMPARISON OF THERMAL EXPANSION BEHAVIOR OF VARIOUS CERAMIC MATERIALS WITH NiAℓ AND FeAℓ.

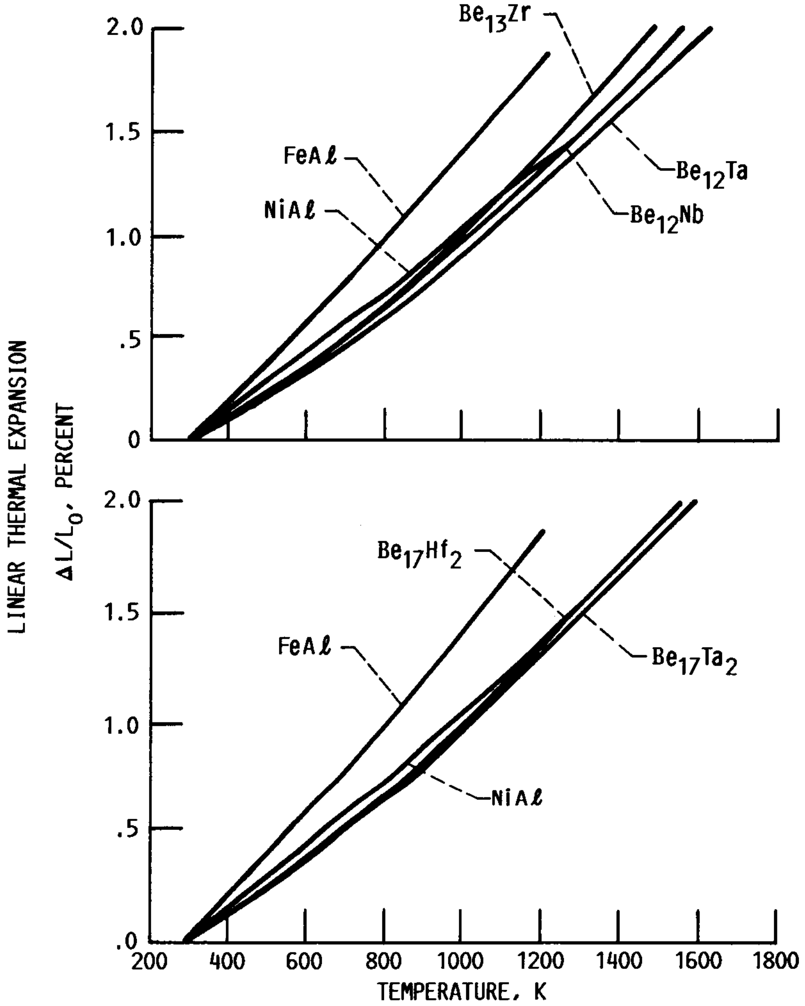

FIGURE 3. - COMPARISON OF THERMAL EXPANSION BEHAVIOR OF BERYLLIDES WITH NiAℓ AND FeAℓ.

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16. Abstract

Several potential reinforcement materials were assessed for their chemical, coefficient of thermal expansion (CTE), and mechanical compatibility with the intermetallic matrices based on NiAl and FeAl. Among the ceramic reinforcement materials, Al_2O_3, TiC, and TiB_2, appear to be the optimum choices for NiAl and FeAl matrices. However, the problem of CTE mismatch with the matrix needs to be solved for these three reinforcement materials. Beryllium-rich intermetallic compounds can be considered as potential reinforcement materials provided suitable reaction barrier coatings can be developed for these. Based on preliminary thermodynamic calculations, Sc_2O_3 and TiC appear to be suitable as reaction barrier coatings for the beryllides. Several reaction barrier coatings are also suggested for the currently available SiC fibers.

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