Part I

Processing

PHASE STABILITY IN PROCESSING OF HIGH TEMPERATURE INTERMETALLIC ALLOYS

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ABSTRACT

In the development of high temperature intermetallics involving various aluminides, silicides and Laves phases, it has become evident that it is essential to consider the strong influence of materials processing throughout all stages. The underlying basis for alloy synthesis, processing and the assessment of thermal stability is established by the relevant phase equilibria, the characteristic diffusivities and the possible solidification reaction pathways. In almost all cases the microstructures of the most useful metallic alloys are multiphase assemblies in which the relative phase fractions, compositions and morphologies play key roles in optimizing the performance under high temperature conditions. The microstructure designs are usually tailored for strength, toughness, creep resistance and environmental stability and involve a balance of features derived from mixtures of a ductile phase and intermetallic phases. There is a clear experience that the level of materials processing can only be as sophisticated as the level of knowledge of the phase equilibria and the underlying kinetics. In many of the contemporary intermetallic alloys the phase stability must be considered in terms of multicomponent equilibria and non-stoichiometric intermetallic compositions. Recent developments in several important intermetallic alloy classes illustrate the guidance into alloy design and processing options provided by systematic studies of phase stability.

INTRODUCTION

Intermetallic alloys are widely recognized as having a large potential for high temperature structural applications. The strongly ordered nature of intermetallic alloys is often reflected in a high melting point which of course is an essential requirement for high temperature service[1]. However, the issues involved in phase stability concern more than just melting point. For example, the high temperature environment also represents an aggressive atmosphere so that oxidation resistance[2] is clearly a concern as well as diffusional interaction with other components. At the foundation of phase stability considerations is the phase equilibria behavior[3]. Careful phase equilibrium studies are always challenging, but they can be especially difficult for intermetallic systems where minor impurity levels can influence behavior and phase transformations involving ordering reactions can alter microstructures from those that represent high temperature equilibrium[4]. Moreover, it is important to recognize that phase stability and microstructural stability refer to complementary, but not identical issues. For example, an alloy with microstructural stability will also exhibit phase stability, but the converse does not necessarily apply. At the same time, the capability to develop controlled modifications of microstructural morphology within the constraints of phase stability are clearly related to the reaction kinetics governing a particular processing pathway[4]. For elevated temperature service it is often the case that the alloy attributes that are desirable for most effective processing are counter to those that are considered to be desirable for optimum performance. Relatively high diffusivities are attractive in processing for homogenization of as-cast segregation or for powder consolidation, but are not desired for creep resistance or environmental stability. Since the performance characteristics usually take precedence, processing ingenuity is an important requirement. For this task the details of phase stability can be critical in identifying acceptable processing paths.

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In addressing a number of mechanical property issues at both ambient and elevated temperatures several strategies have evolved such as those based upon selective alloying of intermetallic phases, use of composite designs and the application of multiphase microstructures[5,6]. Each approach offers a number of attractive features, but these can only be realized after the associated challenges are overcome. For example, attempts to alloy intermetallic phases often proceed on a semi-empirical basis due to limited information on solubility relations and possible constitutional defects. In composite designs, processing issues related to interfacial reactions between the intermetallic matrix and the reinforcements often dominate the observed behavior and can obscure the influence of the intended design. Similarly, the control of phase compositions and relative volume fractions in multiphase microstructures requires some detailed knowledge of the phase equilibria-at least in the composition and temperature domain of interest. Of the different approaches, the latter involving multiphase microstructures has an important experience base in the application of superalloys. Indeed an important lesson that can be obtained from the experience with superalloys is that in multiphase microstructures synergistic interactions between the separate phase morphologies can provide enhanced performance compared to the averaged behavior of the constituents.

A full discussion of all of the phase stability issues involved in processing of intermetallic alloys is not possible within the available coverage. For example, the important advances in electronic structure[7] and first principles analysis[8] methods will not be discussed. Instead certain cases will be examined in order to identify some of the interrelationships between phase stability,microstructures and processing. Attention will be focused on the importance of multiphase microstructures. The special features associated with multiphase microstructures in intermetallic alloys offer challenges and new opportunities to develop unique materials systems and to tailor engineered microstructures.

BACKGROUND EXPERIENCE

The application of phase stability is of considerable importance in the identification and development of microstructures that offer the balance of engineering properties that are required for high temperature service. The classic example of careful microstructural control are the Ni-base superalloys which derive their high performance and versatility from designs that are combinations of a Ni-rich disordered solid solution and an ordered Ni_3Al intermetallic phase. Both the order/disorder relationship of the two phases and the small mismatch in lattice parameter which is optimized by careful composition control are central to the success of superalloys[9,10]. While the strategies that are being applied to intermetallic alloys are intended to yield materials that will replace Ni-base superalloys in some uses, it seems prudent to use the lessons from the superalloy experience in reaching this goal. The basic point of this experience and the value of multiphase microstructures is that the combination of a hard, brittle intermetallic with a softer, more ductile constituent can yield an effective combination of a high strength, creep resistant alloy with reasonable ambient ductility. In the superalloys it is worthwhile to note that the phases are present at high volume fractions and synergistic non-linear effects can develop which permit performance levels to exceed those expected from simple rule-of-mixtures scaling[11]. In addition, selective alloying of specific phases can be essential in controlling phase stability through changes in solvus behavior and other possible transformations over the service range[10]. Moreover, as further support for this approach the evolution of Ti_3Al-based alloys[12] which are a combination of α_2 and β_o phases and the TiAl - based alloys[13] which are a combination of γ and α_2 phases are examples.

The development of multiphase microstructures in intermetallic alloys requires an optimum balance of compositions, volume fractions, sizes and distributions of constituent phases. Clearly, the phase stability information that is summarized in phase diagrams provides essential guidance. For ordered alloys there are also additional reactions such as first and second order phase transitions and

the composition dependence of the transition temperatures as shown in Fig.1[14]. If the coexisting phases exhibit similarities in crystal structure and compatible lattice parameters, then a phase equilibria such as that shown in Fig.1a may develop and allow for the formation of a high volume fraction of a second phase either by a nucleation and growth process or by a spinodal ordering. In addition in ternary and higher order systems the development of other superstructures such as $L2_1$ is possible. When the coexisting phase compatibility is poor, other reaction pathways, including solidification processing, are available and can involve metastable ordering reactions with novel microstructures[15].

There is a growing experience in the exploitation of changing phase stability with processing to develop different types of multiphase intermetallic alloy microstructures. A few examples of the various phase and morphology combinations that have been produced by processing can offer a perspective on the options that are available with this processing route. For example, Naka and colleagues[14,16] have succeeded in developing two-phase microstructures in pseudobinary Fe-Ni_2AlTi and Nb-Ti_2AlMo systems involving A2-$L2_1$ and A2-B2 structures that exhibit morphologies that are similar to the γ/γ' microstructures in nickel-base superalloys (i.e. the disordered phase is the matrix) and show attractive performance including a yield strength which increases with increasing temperature. In order to improve the toughness and creep resistance of NiAl-base alloys, Ishida *et al.*[17] and Jung and Sauthoff[18] developed precipitates of disordered bcc solutions in the B2 matrix and Allen *et al.*[19] employed a spinodal reaction to yield fcc precipitates in NiAl. By varying the composition between NiAl and Ni_2AlTi, Field[20] were able to apply a spinodal ordering reaction to develop a fine- scale precipitation and to change the precipitate phase from Ni_2AlTi in a NiAl matrix to NiAl in a Ni_2Ti matrix. In addition, Dimiduk *et al.*[21] have shown that precipitation of a metastable $L2_1$ phase in an Fe_3Al(DO3) ordered matrix is an effective strengthening method. In a systematic study Nemoto and co-workers[22] examined a number of nickel and titanium aluminide intermetallic alloys with both ordered and disordered precipitate phases. Depending on the precipitate/matrix interface character different types of dislocation/precipitate interactions were observed to contribute to strengthening. An excellent example of a broad - based and detailed effort to understand and apply multiphase microstructures has been documented clearly by Yang, Cahn and co-workers[23-26]. In order to address the limited ductility of NiAl / Ni_2AlTi microstructures, they adopted a strategy of including a third phase, Ni_3Al which is relatively more ductile. Moreover, in order to develop the proper processing, it was necessary to carry out a phase equilibria study which they did by both careful experiments and calculation[24]. The resultant three phase microstructure displayed notable improvements in plasticity of up to 13% in compression at room temperature with excellent high temperature performance (i.e. comparable to that of some superalloys). With a monolithic material the microstructure options are those available by in-situ processing (e.g. through precipitation). While this is not necessarily a serious limitation, additional options can be available by synthesizing microstructures from the constituent phases. The effectiveness of this strategy has been nicely demonstrated by Hsiung and Bhadeshia[27] who used the same alloy system studied by Yang et.al.[24]. In effect, an "intermetallic-intermetallic" composite was fabricated by extrusion to yield a fibrous three phase morphology with the more ductile $Ni_3(Al,Ti)$ phase sandwiched between the Ni(Al,Ti) and the Ni_2TiAl phases. Phase stability was included in the design by employing phase compositions corresponding to the three phase coexistence established in the phase diagram study. The initial evaluation results showed improvement in strength and ductility compared to similar material after in-situ processing. There is clearly much room for processing control with this approach.

Much of the current experience has served to identify the general effectiveness of multiphase microstructures as a means of tailoring the engineering properties of intermetallic alloys. Within this approach there are other options available for further microstructural manipulation. For example, a close attention to microstructural morphology has been shown to be of critical importance in

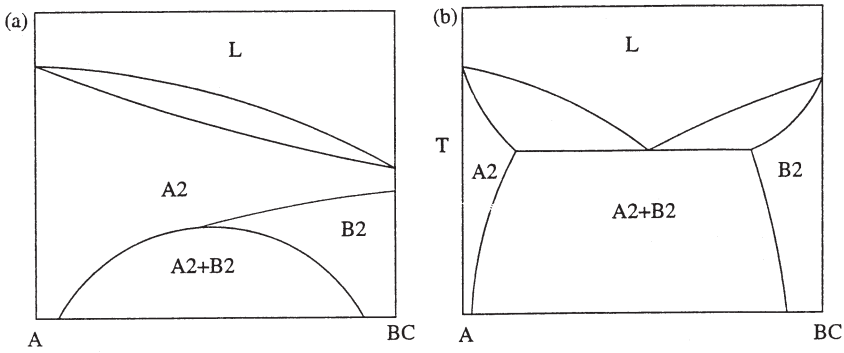

Fig. 1 Schematic phase diagram for precipitation reactions in intermetallic alloys.

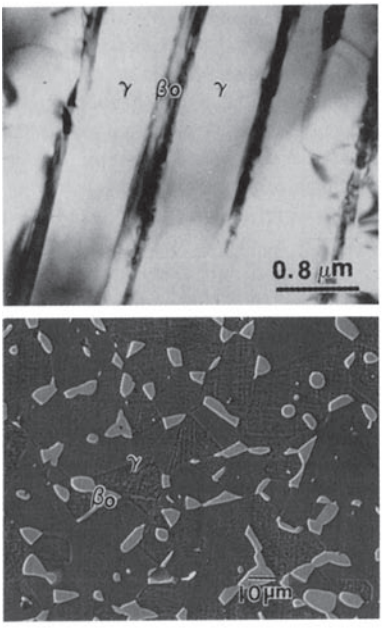

Fig. 2 (a) bright-field TEM image of an annealed(1240°C/150h) showing $\gamma+\beta_o$ lamellar structure and (b) SEM micrograph of an equiaxed $\gamma+\beta_o$ microstructure produced by quenching from 1400°C and annealing at 1175°C for 140h.

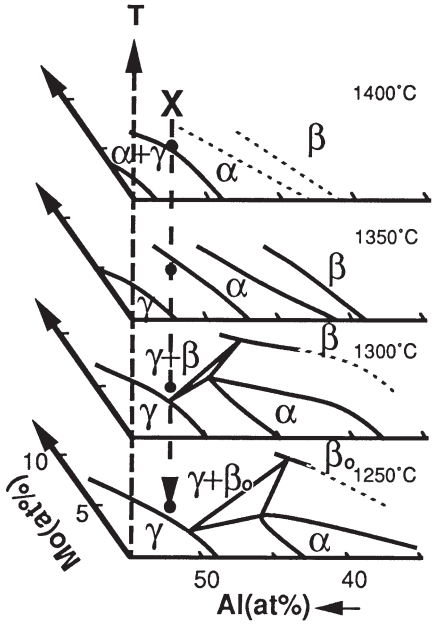

Fig. 3 Partial isothermal sections for Ti-Al-Mo alloys over the temperature range from 1400°C to 1250°C. The $Ti_{45}Al_{50}Mo_5$ composition is indicated by the vertical dashed line.

Ti_3Al[12] and TiAl[14,28] systems. Moreover, for intermetallic phases non-stoichiometric compositions and constitutional defects that can be achieved by processing will have an influence on performance. In order to examine some of these issues further, three examples will be discussed to illustrate the interrelationships between phase stability, processing and microstructural control.

TITANIUM ALUMINIDE ($\gamma+\beta_o$) ALLOY MICROSTRUCTURES

In binary TiAl-base alloys the main microstructural constituents are $\alpha_2+\gamma$ mixtures. As a result of extensive recent efforts it is clear that the important mechanical properties are strongly influenced by the microstructural morphology. For example with conventional ingot processing methods the γ phase precipitates from the high temperature α phase to yield a lamellar structure of alternating plates with crystallographical alignment of the respective close-packed planes and directions. Often following casting the ingots are subjected to hot deformation and annealing. One important option is the duplex structure consisting of fine, recrystallized γ grains, fine lamellar grains and some fine α_2 particles. In general two-phase alloys in polycrystalline lamellar form have poor ductility in comparison to the duplex structure, but superior strength[14]. To achieve a more attractive performance profile further microstructural control together with additional alloying especially with refractory metals such as Cr and Nb has been successful[28-30]. The actual role(s) of the additional alloying is not completely clear, but there is an influence on the relative α_2 and γ phase volume fractions and in some cases a report of the development of a ternary β_o phase based on Ti_2AlX (X= refractory metal) with B2 ordering[31,33]. In binary alloys a $\beta_o+\gamma$ combination is not possible, but with modest amounts of several third elements such as Mo which is a strong β stabilizer, a stable β_o phase develops. There is only limited information available in the literature concerning the details of the phase stability relations in TiAl alloys involving the β_o phase, but there is some work from Japan indicating mechanical property benefits[30]. In order to expand the number of microstructural options available with TiAl, the phase stability relations have been examined in several Ti-Al-Mo alloys.

In the Ti-Al-Mo system the existence of an ordered bcc (B2 or β_o) in alloys near Ti_2AlMo was first identified by Böhm and Löhberg[34]. Other work on the ternary phase equilibria yielded valuable results, but the interpretation at that time was hampered by the absence of reliable phase equilibria for the binary Ti-Al system[35]. More recently the development of a ($\beta_o+\gamma$) two phase field was confirmed by careful examination of the microstructure of a $Ti_{45}Al_{50}Mo_5$ alloy after annealing at 1240°C for 150 hrs[36]. As shown in Fig. 2a the resultant ($\beta_o+\gamma$) microstructure resembles very closely the ($\alpha_2+\gamma$) lamellar morphology. Indeed, the reason for the close similarity is related directly to the phase reactions that develop following cooling after solidification. The basis for interpreting these reactions is illustrated in Fig. 3 which presents a sketch of the governing phase relations in the Ti-Al-Mo system near the Ti-Al binary side over a range of temperatures covered by the reactions. As indicated in Fig.3, at 1400°C the $Ti_{45}Al_{50}Mo_5$ alloy lies in a single α phase field and with cooling enters a two-phase ($\alpha+\gamma$) region where the usual lamellar morphology for ($\alpha+\gamma$) can develop. Upon further cooling, the alloy crosses into a three-phase ($\gamma+\alpha+\beta$) field where β nucleates most likely at γ/α interfaces and then β_o grows to replace α in the original lamellar microstructure.
Once formed this microstructure displays remarkable stability as indicated in Fig. 2a where there has been essentially no microstructural change after 150hrs at elevated temperature. Indeed the microstructural stability is consistent with a detailed TEM study which indicates coherent interfaces between the γ and β_o phases[37].

A very different ($\gamma+\beta_o$) two-phase microstructure can be created in the $Ti_{45}Al_{50}Mo_5$ alloy by starting again in the single phase α field at 1400°C and quenching to suppress precipitation of the

(α+γ) lamellar structure. In this case the as-quenched structure is a supersaturated γ phase that forms polymorphically from α during the quench. Upon annealing at 1175°C, β_o precipitates develop at γ/γ grain boundaries as allotriomorphs and upon further exposure at 1175°C an equiaxed (γ+β_o) is clearly evident in Fig. 2b. Further studies in this system are in progress, but the examples of at least two distinct microstructures has expanded the microstructural options available for TiAl-base alloys.

HIGH TEMPERATURE Mo-Si-B ALLOYS

Even with the remarkable advances in processing and microstructural control, the evolution of TiAl-base alloys towards a viable candidate for elevated temperature service will still involve applications with service temperatures near or below those for Ni-base superalloys due to the melting temperature limitation. In order to achieve a significant increase in operating temperature capability, it is clear that alloys with high melting temperatures (i.e. approaching 2000°C) are necessary[1]. At the same time, for reliable service it is also necessary for the design to offer oxidation resistance. In fact, while there is a fairly wide selection of candidate alloys based on the melting temperature criterion, the requirement for oxidation resistance severely limits the selection. For Ni-base systems, oxidation resistance is provided by adherent Al_2O_3 coatings[38]. Another coating which provides protection especially at elevated temperatures is based on SiO_2 surface layers[38,39].

A notable example of an intermetallic alloy that satisfies both the melting temperature and oxidation resistance is $MoSi_2$ which is used in furnace elements operating at 1600°C in air. However, $MoSi_2$ has serious limitations in low temperature toughness and high temperature creep resistance. To address these issues a toughening and strengthening strategy based on composite designs has been actively pursued with mainly SiC and refractory metal (i.e. W, Nb) reinforcements[40]. While progress has been made with this approach, matrix / reinforcement compatibility is a concern[41]. In fact, the influence of the reinforcements on the oxidation protection offered by $MoSi_2$ is also a problem[42]. Due to the development of several silicide phases with poor oxidation resistance refractory metal phases do not equilibrate directly with $MoSi_2$ and ceramic reinforcements react with $MoSi_2$ to develop ternary phases[43,44]. However, there is an option in the Mo-Si-B system where it is reported that a Mo solid solution and a ternary Mo_5SiB_2 (called T_2) with a $D8_l$ structure are in equilibrium[45]. An examination of the multiphase microstructures that are possible in the Mo-Si-B system yields some insight into the challenges that alloys with high melting temperatures pose to materials processing.

The main published report concerning phase equilibria in the Mo-Si-B is based upon observations of phase formation in annealed powder compacts where there is some concern for complete equilibration[45]. Although the results of the current study of equilibrated arc-melted samples reveals that some modification of the phase boundaries is necessary, the finding of a two phase field between Mo and T_2 has been confirmed as indicated in the 1600°C isothermal section in Fig. 4. A full analysis of the solidification processing in this system will be given elsewhere, but it is useful to consider one important aspect that is clearly illustrated in Fig.5 for the as-cast microstructure in a $Mo_{79}B_{14}Si_7$ alloy. In the Mo-Si-B system the melting temperature trends in the respective binaries yield a liquidus surface that descends from the Mo-B side to Mo-Si and involves several intermetallics in addition to T_2. The microstructure in Fig.5a indicates that several multicomponent solidification reactions have occurred to yield primary Mo solution and secondary phases of Mo_2B, Mo_5SiB_2, and Mo_3Si. Since the alloy composition is actually in the Mo+T_2 two-phase field, major phase changes must occur upon high temperature annealing. After an annealing treatment of the as-cast sample at 1200°C for 150 Hrs the resultant microstructure as shown in Fig.5b does not indicate any significant change from the initial solidification microstructure. In fact, even after annealing at 1600°C for 150hrs. the resulting

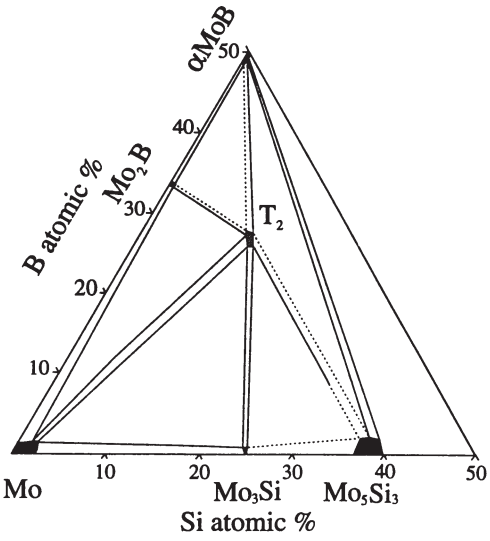

Fig. 4 The Mo-rich portion of the isotherm for the Mo-Si-B system at 1600°C Dotted boundaries are tentative

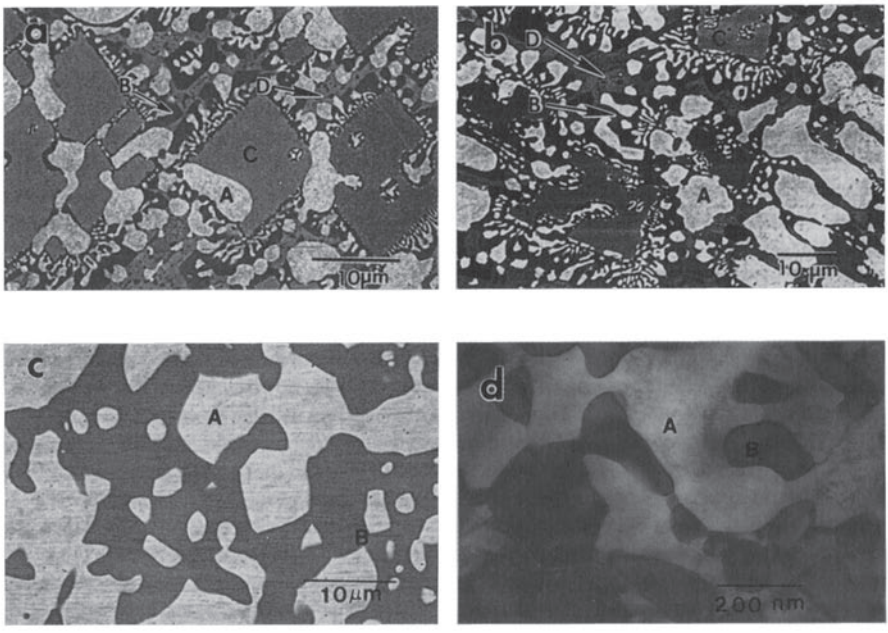

Fig. 5 Influence of processing on microstructures in a $Mo_{79}Si_{14}B_7$ alloy , (a)as-cast , (b) annealed at 1200°C for 150h, (c) annealed at 1600°C for 150h, and bright field TEM image of splat quenched sample. A. Mo , B. T_2 , C. Mo_3Si , D. Mo_2B

150hrs. the resulting (Mo+T_2) microstructure does not exhibit a fully equilibrated morphology, due to the sluggish diffusion in this system. Based upon the observed microstructural changes at 1600° C, an estimate of about 10^{-18} m^2/s can be made for the diffusivity. This experience is a good example of a major challenge in the processing of high temperature materials. The desired attributes for high temperature service of low oxidation rate and creep resistance are related to diffusion rates which must be low for good performance. However, the same diffusion characteristics clearly govern the attainment of phase and microstructural equilibrium; thus these processes will also be slow.

In order to address the opposing demands of performance and processing, a modified processing approach is necessary. This has been successfully achieved with rapid solidification methods which allow for the suppression of solidification segregation which yields the Mo_2B and Mo_3Si phases. As indicated in Fig.5d the fine scale of the as-splat microstructure which exhibits the (Mo+T_2) phases will equilibrate more readily than the coarse structure(Fig.5a). Since the experience in the Mo-Si-B system is likely to be repeated in other multicomponent elevated temperature intermetallic alloys, rapid solidification methods will be an effective approach to the equilibrium phase stability in such systems.

INFLUENCE OF ALLOYING EFFECTS — LAVES PHASE INTERMETALLICS

The ordered nature of intermetallic alloys introduces several structural aspects of phase stability that are not involved in the usual assessment of alloy phase stability. For example, constitutional point defects (e.g. vacancies, antisite atoms, and triple defects) that are associated with non-stoichiometric compositions can reach high concentrations compared to disordered phase behavior. Similarly, antiphase boundaries and the specific characteristics of dislocations and their motion are unique to ordered alloys and are different for different structural types. All of the special structural features of ordered alloy phases are influenced by additional alloying which can often be site specific in that certain elements tend to occupy sites on a given sublattice in the ordered structure. In one extreme, additional alloying can act to destabilize an existing structure in favor of another when non-stoichiometry is unfavorable such as the transformation of Al_3Ti with the DO_{22} structure into a cubic $L1_2$ phase with certain solutes[46]. The attempts to analyze this form of structural stability range from traditional methods based on electron to atom (e/a) ratios and relative atomic size (D_a/D_b) ratios to contemporary methods based on electronic structure considerations[9,10]. While each approach has had a measure of success, the often relatively small energy difference between competing structures presents a challenge to any analysis. In the more common application, additional alloying is used to fine tune microstructural characteristics as with the Ni-base superalloys[47].

The influence of alloying on structural stability can be significant in strongly ordered intermetallics where the disturbance in the atomic arrangement may involve changes in defect sensitive properties. An example of this behavior can be illustrated with the Laves phases based on the C14, C15 and C36 structures which represent one of the most populous intermetallic classes and have been receiving more attention recently. Excellent evaluations of the potential and progress in the understanding of Laves phases can be found in the reviews by Livingston[48,49]. One of the important trends in this work has been the recognition of the value of multiphase microstructures as an effective method of providing a metallurgical control of the mechanical properties[50-54]. In fact, Livingston has made special note of several systems where the combination of a ductile phase (usually bcc) and a Laves phase has yielded impressive performance in terms of mechanical properties. Also, there is evidence that in these multiphase designs, the Laves phases in certain alloy systems can exhibit significant plastic deformation which suggests that Laves phases are not inherently brittle[49].

The abundance of Laves phase structures has often been attributed to geometric factors involving atom close packing, symmetry and metallic bonding[55]. Indeed all Laves phase structures can be constructed from six basic stacking arrangements involving close-packed planes in the close-packed