A new method is developed for preparing Ti$_5$Si$_3$/TiAl \textit{in situ} composites by incorporating metastable phases (called metastable precursors) into TiAl (a mixture of elemental Ti and Al) matrix powders. Metastable precursors with a starting composition of Ti-14Al-21Si are prepared by mechanical alloying (MA). They have been proven through X-ray diffraction (XRD) analysis and transmission electron microscope (TEM) observations to be mainly consisting of mixtures of nanostructured solid solutions and milling-formed TiAl compound. Particularly, phase reactions and transitions in the precursors and the composites during heating have been investigated in detail by using diffraction thermal analysis (DTA) in conjunction with XRD. It has been found that Ti$_5$Si$_3$ is \textit{in situ} formed through a phase transition chain, TiSi$_2$ \textit{\rightarrow} Ti$_3$Si$_4$ \textit{\rightarrow} Ti$_5$Si$_3$. When the composite powder (precursor, Ti and Al) is heated, a combustion reaction first occurs in the matrix, which results in the formation of TiAl$_3$ and/or TiAl followed by the completion of the previously mentioned silicide transitions in a very short time. Scanning electron microscope (SEM) observations indicated the locations of reinforcements in the reaction-formed composite, and TEM observation provided some details of the structures for the reinforcements and their neighborhood. This method is intriguing because a designed phase hierarchy is possible.

**I. INTRODUCTION**

The TiAl-based composites have been widely investigated due to their potential use in high-temperature applications such as aerospace engines. Major focus was on particulate-reinforced TiAl composites due to the availability of multitude of cost-effective techniques. Both the external addition and internal formation (\textit{in situ}) of second phases, such as ceramic and/or ductile phases in TiAl matrix that are widely used for producing two-phase materials, have been used to improve the room-temperature ductility and high-temperature properties of TiAl-based materials. But \textit{in situ} formation is more appealing in TiAl composite syntheses because of the attainment of many beneficial effects in properties, which arise mostly from the development of a "tolerable" interfacial structure in the composite. Significant efforts toward microstructural control of TiAl alloys have been made via the use of a composite route, by which the microstructures can be expected to be designed (or fine-tuned) as in the case of other materials.

Mechanical alloying (MA) has been used to prepare TiAl compounds either their potential use or fully metastable or in-between. To maintain a metastable state, however, the processing temperature should be somewhat lower than usual. The benefits of instability of metastable phases as well as the ability of maintaining them in stability are to be proven. It is of practical interest to know when the metastable phases are unstable and will transform into useful stable phases with energy release when heated to a higher temperature. Such an "unstable environment" can be realized by putting the metastable phases into a reactive system in which an exothermic reaction would occur. For the latter case, however, the efforts are on the utility of keeping metastable phases in stability to develop structures for improving the toughness of materials, for example, amorphous reinforcements in a composite.

Elemental Ti and Al (in powder form) will react to form TiAl compound (Ti$_3$Al or TiAl or TiAl$_3$) if the ignition temperature is reached. This reaction is exothermal and proceeds in a combustion mode with tremendous heat release within a short time (normally a few seconds). The combustion temperature can be as high as 1270°C. Another interesting feature is that such a reaction may lead to other phase transitions in a cascading way that may result in the creation of intriguing microstructures.

Both TiAl and Ti$_5$Si$_3$ phases are stable at elevated temperatures, suggesting the possibility of developing Ti$_5$Si$_3$/TiAl composites for high-temperature applications. Perepezko et al. studied \textit{in situ} reactions in TiAl (\textit{y}TiAl, Ti$_3$Al)-TiSi$_2$ diffusion couples using the "kinetic biasing" strategy. The formation of a Ti$_5$Si$_3$ phase was pertained to a Ti layer that was used as a kinetic bias inserted between TiAl and TiSi$_2$ couples. However, the hierarchy of phase formation and sequence may be different if Ti$_3$Si$_3$ forms as a result of complex reactions in a short time (if TiAl is combustion-formed) rather than a slow diffusional process.

In this research, a new method has been employed for preparing \textit{in situ} Ti$_5$Si$_3$/TiAl composites. Metastable precursors are incorporated instead of external addition of Ti$_5$Si$_3$ or reactant elements such as Si into TiAl matrix (both Ti and Al are in elemental powders) \textit{via} uniform blending. Subsequent heating of the powder mixture will result in the formation of Ti$_5$Si$_3$/TiAl composites. These precursors are
Precursors were synthesized by the MA process. Initial powders used for this experiment are pure Ti, Al, and Si, with average particle sizes of 25, 13, and 71 μm, respectively. The powders of the selected composition were put into a steel vial together with steel balls at a ball-to-weight ratio of about 20:1. The vial was sealed by a rubber O-ring, filled with argon gas, and installed on a planetary ball milling machine. The MA process was carried out at a medium speed only to avoid any sticking of powder to the milling tools, a phenomenon frequently reported by other performers. The milling process was interrupted at some predetermined intervals for sampling, and the total time of milling was 100 hours. Two vials were simultaneously installed on the same milling machine at opposite positions. Powders from one vial were used for further analyses, and those from the other were used as precursors for composite formation.

Powders for use as matrices were produced by blending the elemental Ti and Al powders in a mixer under the protection of argon gas. The composite powders were also prepared in this manner.

X-ray diffraction analysis was conducted on a Kristal-loflex 121127 type diffractometer affiliated with SIEMENS*

*SIEMENS is a trademark of Siemens Electrical Equipment, Toronto.

software, using a voltage of 35 kV, a current of 30 mA, and Cu Kα radiation. Differential thermal analysis (DTA) was performed on a PERKIN-ELMER** 7 series using DTA 7 section in DSC mode. The heating rate was 20 °C/min and the sample was argon-protected during heating. All samples for XRD and DTA are in powder form. Some of the samples were also examined using two kinds of analytical electron microscopes (TEMs). PHILIPS‡ CM20 for milled powders

‡PHILIPS is a trademark of Philips Electronic Instruments Corp., Mahwah, NJ.

and EM420 for reactive formed bulk samples, both with a working voltage of 100 kV. A scanning electron microscope (SEM) (JSM-6301F, cold-field emission) was employed to locate the silicide positions in the reaction-formed composites and in situ analyzed the phase composition with ZAF correction using an affiliated X-ray energy dispersive (EDS) installation.

Also, the mechanical properties of the monolithic and composite materials formed were evaluated using simple cylindrical compression tests. Samples used for the tests were machined from the powder compacts into cylinders of 6.5 mm in height and 4.5 mm in diameter and were compressed until fracture occurred.

III. RESULTS AND DISCUSSION

A. Formation of Metastable Precursors by MA

Figure 2 shows the XRD results of Ti-14Al-21Si powders before and after ball milling. The initially sharp diffraction peaks (Figure 2(a)) are considerably broadened after ball milling (Figures 2(b) and (c)) due to the refinement of the grain size and the possible establishment of atomic level strains. Further analysis by XRD software showed that the average grain size for each element (elemental Ti, Al, Si,