Chapter 1: Introduction

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1.1 Mechanical Alloying and Nanotechnology

Mechanical alloying (MA) by high-energy ball milling has turned out to be a versatile processing route for preparing nanostructured composites and intermetallics with a broad range of compositions and structures. High-energy ball milling is also able to produce nanostructured elemental powder and the process is called mechanical milling (MM) (Gleiter, 2000; Fecht, 1995). During mechanical milling or mechanical alloying, the powder particles are subjected to repeated fracture, fragmentation and cold welding under the impact of grinding balls and when the process continues for a long time, nanocrystalline or amorphous structure can be generated (Fecht, 2001; Fecht and Ivanisenko, 2007; Koch, 1993; Suryanarayana and Koch, 2000). During extensive deformation of the powder particles, enhanced diffusion of the ingredients also takes place and the process is termed as mechanical diffusion. This enables formation of alloys at near ambient temperature of the milling atmosphere (Balluffi and Rouff, 1962; Inoue, 1995; Suryanarayana, 1995, 2001; Suryanarayana et al., 2001; Bhadeshia, 2000, 2005; Pabi et al., 1998).

W has a very high melting temperature (3422^{o}C), high elastic modulus (Young's modulus = 411 GPa), high density (19.25 g/ml) and low coefficient of thermal expansion (4.5 x 10^{-6} K^{-1}). It can potentially be a very important high temperature structural material (Lassner and Schubert, 1999). However, the study on the W-based alloys is rather difficult because of its high melting point and the need of hydrogen atmosphere for its processing. From this point of view, MA being a near ambient processing method, can provide a good proposal for the study on some W-based liquid phase sintered alloys popularly known as tungsten heavy alloys (WHA) (Hong and Ryu, 2003; Ryu and Hong, 2003; Suri et al., 2009).

1.2 Tungsten Heavy Alloys (WHAs)

The main component of tungsten heavy alloys (WHAs) is about 90-98 wt. % W and in order to use the high-density property of the W, along with the addition of Ni and Cu or

Ni and Fe, etc. to enhance the sintering property and processability. It has a very high density of around 16 - 18.5 g/ml. WHAs possess excellent mechanical properties such as high tensile strength of 800 to 1200 MPa and elongation percentage of 20 to 30 %. Its main application is for making rotors of dynamic inertial materials, stabilizers of aircraft wings, shielding materials for radioactive materials, containers in hospitals for radioactive isotope (Cobalt 60), and for material of armour piercing bullets and moulds. Uranium based alloys are the other candidate for these applications; but they are eliminated due to toxicity considerations and being a potential health hazard (Upadhyaya and German, 1998; Das et al., 2009; Ryu et al., 1997, 2000; Hong and Ryu, 2003; Ryu and Hong, 2003; Huang and Mashimo, 2000; Cho et al., 1993; Gurland, 1958; Hong et al., 2002; Akhtar, 2008; Koch, 1997).

The majority of current uses for WHAs are best satisfied by the W-Ni-Fe system. Alloys such as 93 W - 4.9 Ni - 2.l Fe (wt. %) and 95 W - 4 Ni - l Fe (wt. %) represent most common compositions of WHAs. There are also a number of alloy systems currently in the various stages of development for kinetic energy penetrators that are intended to provide a WHA that will undergo failure under high deformation rate by shear localization.

1.3 Background of the Present Investigation

It may be pointed out that conventional micrometer sized elemental W particles require a very high sintering temperature (> 2700^{o}C) for processing. In order to reduce the sintering temperature to about 1500^{o}C, elements like Cu, Ni, Al, and Fe, which are almost insoluble in solid W, may be added to W to promote liquid phase sintering. Nanostructuring the ingredient powders in this case may have a good prospect of lowering the sintering temperature, because experiments on other systems have shown that presence of a very high fraction of internal and external surfaces can reduce the sintering temperature by about 300-500^{o}C (Groza, 2007). Recent work of Malewar et al. (2007) has shown that the sintering temperature of elemental W can be remarkably reduced to about 1790^{o}C from conventional 2700^{o}C by nanostructuring the W by prior mechanical milling. Present work has attempted to develop W-Cu nanocomposites and a new WHA, i.e., W-Ni-Al through MA followed by sintering.

W and Cu are mutually immiscible elements in solid state or even in liquid state under equilibrium conditions (Massalski and Okamoto, 1990; Brandes and Brook, 1992). Comparatively low melting temperature of Cu (1083^{o}C) can help in sintering the W-Cu nanocomposites. MA by high-energy milling is a non-equilibrium processing route, which often shows the extension of the solid-solubility limit. In the present investigation, an attempt has been made to synthesize W-Cu nanocomposites by MA. The thermal stability of the milled product and their sintering characteristics have been investigated.

Work on W-Ni-Al system has been undertaken with the objective of reinforcing W with nickel aluminides. The wide difference in the melting temperatures of W (3422^{o}C), Ni (1455^{o}C) and Al (660^{o}C) would pose difficulty in sintering of W-Ni-Al alloys through conventional routes. In the present study MA characteristics of binary W-Al and W-Ni systems have been first investigated for understanding of their MA characteristics, which would be useful in the study of MA of ternary W-Ni-Al system. Here attempt has been made to synthesize the nickel aluminides in-situ in W by MA or nickel aluminides synthesized ex-situ at ambient temperature through MA have been added to W and subsequently milled again. In conventional WHAs relatively low melting point elements like Ni (1455^{o}C) and Fe (1510^{o}C) are added to W to promote liquid phase sintering at a moderate temperature (≤ 1600^{o}C). On the other hand, NiAl is a well-known high temperature structural material because of its low density (5.86 g/ml), high melting point (1638^{o}C), good oxidation resistance (up to 1300^{o}C) and good thermal conductivity. Similarly Ni_3Al also exhibits high hardness, high melting temperature (1390^{o}C), low density (7.26 g/ml), good oxidation and corrosion resistance (Moshksar and Mirzaee, 2004; Enayati et al., 2004). It remains to be seen, whether these intermetallics, which have been synthesized in-situ or added after synthesizing them externally, can act as the sintering promoter in nanostructured W. NiAl and Ni_3Al have much superior high temperature properties compared to Fe and Ni, and hence there is a possibility to improve upon the performance of the WHA to a great extent as compared to the traditional WHAs like W - 7 wt. % Ni - 3 wt. % Fe.

1.4 Scope and Objectives of the Present Study

The present study explores MA as a route for synthesizing W-Cu, W-$Ni_{50}Al_{50}$/NiAl and W-$Ni_{75}Al_{25}$/Ni_3Al nanocomposites. The major objectives of this work were as follows:

a. To synthesize various nanocomposites of W-Cu, W-$Ni_{50}Al_{50}$/NiAl and W-$Ni_{75}Al_{25}$/Ni_3Al systems by MA.

b. To find out the possible extension of the solid solubility of Cu, Ni and Al in W during MA of the binary W-Cu, W-Al and W-Ni systems. These elements are sparingly soluble in W.

c. To track the formation of nickel aluminides, namely, NiAl and Ni_3Al, in-situ in the various compositions of W-$Ni_{50}Al_{50}$ and W-$Ni_{75}Al_{25}$ elemental blends during the course of milling and subsequent heat treatment of the milled products have been characterized.

d. To study the growth of the crystallites during annealing of the mechanically alloyed powder.

e. To compare the sintering characteristics of the nanocomposites developed here with a standard WHA (W - 7 wt. % Ni - 3 wt. % Fe) synthesized in a similar fashion to explore the viability of using nanostructured Cu or nickel aluminides as the sintering aid to nanostructured W.

1.5 Brief Layout of the Thesis

The whole thesis has been divided into 7 chapters. **Chapter 1** here has provided a brief introduction to the subject and aim of the present study.

In **Chapter 2** of this thesis a comprehensive literature review in the area of investigation has been presented. **Chapter 3** specifies the experimental details. In **Chapter 4** of this thesis, the results and discussion of MM of elemental W and MA of W-Cu system have been reported. Thermal stability of milled elemental W and W-Cu nanocomposites has also been reported in this chapter. The MA of binary W-Ni and W-Al systems has been studied to facilitate the understanding of the MA characteristics of the ternary W-Ni-Al system. **Chapter 5** reports the findings of the MA of binary W-Al system whereas **Chapter 6** reports the findings of the MA of binary W-Ni system.

One of the major objectives of this work was to explore the possibility of replacing the conventional liquid phase sintered alloy W-Ni-Fe by W-Ni-Al system, where the nickel aluminides at the sintering temperature may possibly serve as the sintering promoter as well as the strengthening agent at the service temperature. In **Chapter 7** of this thesis, we have discussed the results of W-Ni-Al system developed by MA followed by sintering.

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