



DEVELOPMENT AND CHARACTERIZATION OF W-BASED NANOCOMPOSITES PREPARED BY MECHANICAL ALLOYING

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ABSTRACT

The present study deals with the synthesis of nanocomposites of W-Cu, W-NiAl and W-Ni₃Al by high-energy ball milling of elemental blends of W, Cu, Ni and Al. Mechanical alloying has been carried out in a Fritsch Pulverisette P-5, using WC milling media. The ball-milled powders have been characterized using XRD, TEM and SEM. The crystallite size and strain in the nanocomposites has been calculated from the x-ray diffraction plots using Voigt's peak profile analysis. The results indicate that nanocomposites with excellent homogeneity can be synthesized by mechanical alloying. The grain coarsening tendency of the nanocomposites after annealing have also been studied. Lattice parameter calculations in all the systems have been carried out both after milling and heat-treatments. The sintering behavior of the nanocomposites has also studied.

Keywords: Mechanical Alloying, Nanocomposites, grain coarsening, sintering

1. INTRODUCTION

High-energy ball milling (mechanical alloying) induces high-energy impacts on the charged powder by collision between balls and particles causing severe plastic deformation, repeated fracturing and cold welding of the particles leading to nanocrystalline materials [1,2]. Mechanical Alloying (MA) of powder particles has turned out to be a versatile alternative to other processing routes in preparing nanoscaled alloys, composites and intermetallics with a broad range of composition and structures in recent years. MA is a solid-state technique and is especially useful for fabrication of those compounds that are difficult to prepare by conventional processes due to high vapour-pressure or large differences in the melting temperature of the components. Moreover in MA the process is carried out at room temperature [3,4].

2. EXPERIMENTAL DETAILS

A Fritsch Pulverisette –5 planetary mill was used. Milling was done in tungsten carbide vials using tungsten carbide balls. The ball weight to charge weight ratio was 10:1. Milling was done at 300 RPM in wet medium in the presence of toluene to prevent oxidation and agglomeration of the charge. X-ray diffraction was done in a Phillips a diffractometer. A JEOL JSM 5800 scanning electron microscope and Phillips transmission electron microscope was used for microstructural characterization. Crystallite size and R.M.S strain was determined from the X-ray diffraction plots using Voigt's peak profile analysis. Precise lattice parameter was determined from the XRD plots using Nelson-Riley extrapolation method.

3. RESULTS AND DISCUSSIONS

3.1 Nanocomposites in W-Cu System

W and Cu are two immiscible elements under equilibrium conditions. Tungsten and Copper are immiscible even in liquid state to a large extent. All the three Hume-Rothery rules are violated in this case. First of all Cu is FCC and W is BCC. The difference in their atomic radii is >20% and the electronegativities are also far apart (Cu=1.9 and W= 2.36). The immiscibility of Cu and W is also reflected in their heat of formation, which is positive (35 kJ/mol).

Several researchers have done work on tungsten-copper or copper-tungsten nanocomposites developed by mechanical alloying. Raghu et. al. have worked on copper-tungsten systems [5]. They synthesized various Cu-W alloys and developed an ultra-fine microcomposite structure of tungsten in a copper matrix by mechanical alloying. Their paper reported that the milling behaviour was dependent on the composition, milling time and milling atmosphere. They also reported that crystallites were in the nanocrystalline region. Costa et. al. [6] reported on the influence of the dispersion technique on the characteristics of W-Cu powders and on sintering behaviour in powder technology. They reported that the dispersion of the copper phase and the fineness of the tungsten phase mostly influenced the sinterability of W-Cu powders. As stated in their paper, using high energy milling produces particles containing very fine tungsten grains embedded in copper, called composite particles. A powder consisting of copper particles dispersed in a very fine tungsten phase improves significantly the sinterability of the W-Cu system in both solid and in liquid states. Relative densities above 94% were easily reached for such powders at temperatures above the Cu melting point and for Cu contents as low as 19% in volume, even for short sintering times. Kim et. al. [7] reported that, after sintering, copper pools are formed outside mechanically alloyed powders. Due to these copper pools, the relative sintered density of more than 95% was achieved by particle rearrangement during liquid-phase sintering. According to their study, the critical temperature of sintering was equal to the Cu melting temperature, and the highest homogeneity and distribution of W and Cu phases was achieved at 1200°C.

Fig. 1 is the XRD pattern from W-20wt.% Cu milled up to various times. They show that both W and Cu become nanocrystalline after about 20 hours of MA. The crystallite size of W and Cu both reach 10-40 nm after 20h of MA (verified by Voigt's relation). Broadening of tungsten and copper X-ray peaks takes place due to the extensive deformation and reduction in crystallite size that takes place during MA. The X-ray analysis shows peaks of WC too. This is due to the wear of grinding media (vial and balls), which are made of WC. From fig 2(a) we can also see the effect of cushioning of ductile Cu in W-Cu system. Copper being more ductile absorbs a high fraction of impacts from the balls and prevents tungsten from breaking down to very low crystallite size. This is why we can see clearly from this figure that crystallite size of W in W-30wt. %Cu is higher than the crystallite size of W in W-10wt. %Cu, as higher weight percentage of Cu has more cushioning effect.

MA is a non-equilibrium process. Diffusion of a small amount of second phase is possible by high-energy milling into the primary phase. Although W and Cu are immiscible diffusion of a small amount of Cu into W is possible during high-energy milling. Precise lattice parameter measurement of W at regular intervals of milling has helped in confirming this fact [8]. Fig. 2(c) shows that there is a significant lowering of lattice parameter of W in W-10wt. %Cu on milling for 20 hours. This is due to the shrinkage of tungsten lattice on dissolution of copper into the tungsten lattice after milling.

3.2 Nanocomposites in W-Ni₅₀Al₅₀ system

NiAl is a well-known high temperature structural material because of its low density, high melting point, low oxidation resistance and good thermal conductivity. NiAl also has a major drawback, as it is very brittle [9]. NiAl was first prepared by Ivanov et.al. [10]. They studied MA of Ni-Al system. Ordered NiAl was formed within 10 hours of milling. Atzmon also found that NiAl can be formed by MA by self-sustained reaction in individual particles and is also accompanied by release of large amount of energy [11]. Efforts have been made here to make use of these good qualities of NiAl by making nanocomposites with tungsten. In this study we investigated the feasibility of preparing W – 10, 20, 30 wt.% $\text{Ni}_{50}\text{Al}_{50}$ nanocomposite by mechanical alloying of Ni, Al and W powder mixtures. It is expected that adding higher percentages of $\text{Ni}_{50}\text{Al}_{50}$ will lead to the formation of ordered NiAl during the process of milling with tungsten.

XRD plots of W-10, 20,30 wt.% $\text{Ni}_{50}\text{Al}_{50}$ as-milled and heat-treated systems shows that NiAl could be formed during milling only when higher weight percentages of $\text{Ni}_{50}\text{Al}_{50}$ was added to tungsten. During heat-treatment the NiAl peaks seen in the XRD plots of W-20, 30 wt.% $\text{Ni}_{50}\text{Al}_{50}$ becomes more intense. W-10wt.% $\text{Ni}_{50}\text{Al}_{50}$ does not lead to the formation of NiAl during milling or heat-treatment.

Comparing fig.2 (a) and fig.4 (a) it can be seen that crystallite size of W in W- $\text{Ni}_{50}\text{Al}_{50}$ is much lower than the crystallite size of tungsten in W-Cu as milled system This is due to the brittle nature of NiAl. Cu being ductile prevents tungsten from breaking down to very low crystallite size whereas NiAl being brittle has very low cushioning effect.

Fig.4(c) shows that there is decrease in the lattice parameter of tungsten when milled with low weight percentage of $\text{Ni}_{50}\text{Al}_{50}$. This is due to the possible diffusion of Ni and Al into the W lattice during milling.

3.3 Nanocomposites in W- $\text{Ni}_{75}\text{Al}_{25}$ system

Ni_3Al is an intermetallic compound, which is excellent in high-temperature strength and oxidation resistance. The strength increases with the increase of temperature unlike ordinary metallic materials. Alloys containing Ni_3Al could be used for high temperature applications. However, the major drawback with Ni_3Al is that it is extremely brittle [12]. Here we have also tried to make W- $\text{Ni}_{75}\text{Al}_{25}$ nanocomposites by mechanical alloying. W-10, 20, 30wt.%- $\text{Ni}_{75}\text{Al}_{25}$ nanocomposites have been prepared by MA. Formation of Ni_3Al was not seen in any of the as milled samples of W-10, 20,30wt. % $\text{Ni}_{75}\text{Al}_{25}$ (fig. 5). But heat-treatment of W-20, 30wt.% $\text{Ni}_{75}\text{Al}_{25}$ at 400,600 or 800°C for 2 hours led to the formation of Ni_3Al (fig. 11). Ni_3Al was not formed during milling in any of the W- $\text{Ni}_{75}\text{Al}_{25}$ systems. Ni_3Al could be formed only on heat-treatment of as-milled W-20, 30 wt.% $\text{Ni}_{75}\text{Al}_{25}$ systems. Low weight percentage of $\text{Ni}_{75}\text{Al}_{25}$ was not favourable for the formation of Ni_3Al either during milling or on subsequent heat-treatment.

3.4 Thermal Stability of W-based Nanocomposites developed by MA

W-10, 20, 30 wt.%Cu milled for 20 hours was also heat-treated similarly for 2 hours at 400,600,800°C. X-ray diffraction patterns showed peaks of tungsten oxide (WO_3) and Copper oxide (Cu_2O) (fig. 8(a)). This is due to oxidation of tungsten by undesired oxygen that went into the furnace tube during heat-treatment. Heat treatment resulted in grain growth. From fig.8 (b) it can be clearly seen that the crystallite size of tungsten is greater than its corresponding as-milled state and increases with the increase in heat-treating temperature. Coarsening of crystallites or grains takes place by diffusion process during heat-treatment. Also from the fig.8 (b) it can be seen that the crystallite size of tungsten in W-20, 30 wt.%Cu as-milled sample increases

profusely on heat treatment as compared to as milled elemental tungsten or W-10wt.%Cu system when heat treated. In elemental tungsten or W-10wt. %Cu as-milled system tungsten absorbed more strain during milling as compared to W in W-20, 30%Cu and on subsequent heat treatment it was more difficult for the W crystallites to grow due to this higher strain. Strain has an adverse affect on heat treatment. Like as milled elemental tungsten W-10wt. % Cu shows almost no variation in crystallite size. Crystallite size of tungsten in W-20wt.% Cu increased from 31nm to 109 nm and in case of W-30wt.%Cu from 32 nm to 137 nm when heat-treated at 800°C for 2 hours.

Heat-treatment does not result in any new phase formation, as W and Cu are immiscible even in liquid state. Heat-treatment also brought the lattice parameter of W to its original value of that of elemental W (3.1652°A). This tells us that the strain absorbed in the W lattice during milling is relieved on heat-treatment. Also any dissolved Cu during milling comes out of the W lattice during heat-treatment.

XRD pattern in fig.10 (a) clearly shows the evolution of NiAl phase after heat-treatment at 800°C in W-20wt.%Ni₅₀Al₅₀. This phase had a very faint peak in the as milled samples of any of the W-20wt.% Ni₅₀Al₅₀. Several peaks of Ni and Al which were not visible in as milled sample were visible after heat treatment for 2 hours at 600°C or 800°C.

XRD pattern in fig.11 shows that heat-treating samples of W-20wt.% Ni₇₅Al₂₅ results in the formation of Ni₃Al phase. This phase was not evident in the as-milled samples of any of the W-10, 20, 30wt.% Ni₇₂Al₂₅.

3.5 Sintering of as milled W-Cu, W-Ni₅₀Al₅₀ and W-Ni₇₅Al₂₅ nanocomposites

All samples were cold-ompacted under a load of 419MPa and were subsequently sintered at 900°C for 2 hours. Sintering of W-20wt.% Cu as milled samples showed the formation of copper rich areas in the tungsten matrix (fig.9). Sintering of as milled W-Ni₅₀Al₅₀ and W-Ni₇₅Al₂₅ samples showed large a fraction of porosity as can be seen in fig.12 (a) and (b) respectively.

4. CONCLUSION

1. Nanocomposites of W-Cu, W-NiAl and W-Ni₃Al have been synthesized by MA of elemental blends of W, Cu, Ni and Al in the composition range of 10-30wt.% of second phase.
2. Crystallite size of 10-40nm has been confirmed in all systems after 20 hours of milling from the XRD peak profile analysis using Voigt's function. Cu, which is ductile, because of its cushioning effect gives higher crystallite sizes of W in W-Cu systems. On the other hand in case of W-Ni₅₀Al₅₀ and W-Ni₇₅Al₂₅ system tungsten shows lower crystallite sizes due to the brittle nature of NiAl or Ni₃Al. It should be noted that major reduction in crystallite sizes occurs after 5 hours of milling in both the systems.
3. As milled elemental W and W-10wt. %Cu or Ni₅₀Al₅₀ or Ni₇₅Al₂₅ showed almost no growth in crystallite size during heat treatment. Due to no second phase or very less amount of second phase there is large amount of strain in W crystallites in as milled elemental W, W-10wt.%Cu or Ni₅₀Al₅₀ or Ni₇₅Al₂₅ systems. During the process of heat-treatment the grain coarsening is restricted by the presence of higher strain in these nanocomposites

4. Addition of 10wt.% $\text{Ni}_{50}\text{Al}_{50}$ to W does not show any NiAl peak during milling or subsequent heat-treatment at 800°C for 2h. This is mainly due to the low amount of $\text{Ni}_{50}\text{Al}_{50}$ in the vial during milling with tungsten. But adding 20,30 wt.% $\text{Ni}_{50}\text{Al}_{50}$ to tungsten gives sharp peaks of NiAl on heat-treating the 20 h MA samples at 800°C for 2 h. Peaks of Ni_3Al were not visible in the X-ray diffraction plots of any of the W-10, 20, 30wt.% $\text{Ni}_{75}\text{Al}_{25}$ systems. But the XRD plots of heat-treated W-20, 30wt.% $\text{Ni}_{75}\text{Al}_{25}$ 20 h MA samples showed prominent Ni_3Al peaks.
5. In W-Cu, W- $\text{Ni}_{50}\text{Al}_{50}$ and W- $\text{Ni}_{75}\text{Al}_{25}$ as-milled system it was seen that the lattice parameter of tungsten decreased when milled with low amount of Cu, $\text{Ni}_{50}\text{Al}_{50}$ or $\text{Ni}_{75}\text{Al}_{25}$ due to the possible diffusion of Cu in W-Cu system or Ni and Al in W- $\text{Ni}_{50}\text{Al}_{50}$ or W- $\text{Ni}_{75}\text{Al}_{25}$ system into tungsten when added in low percentage with tungsten. Heat-treatment of as-milled samples showed relaxation of the lattice of tungsten and the lattice parameter of tungsten goes back to its original value of elemental tungsten (3.1652Å) due to the release of strain from the tungsten lattice on heat-treatment and also because of any dissolved Ni or Al coming out of the tungsten lattice.

5. REFERENCES

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FIGURES

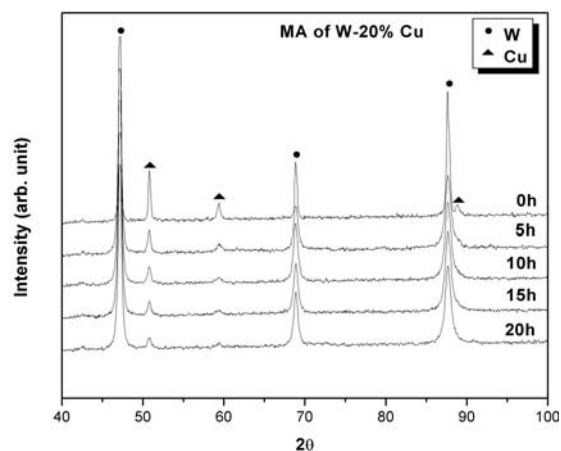


Fig. 1 XRD (Co K α) patterns of mechanically alloyed W-20wt. % Cu as a function of milling time.

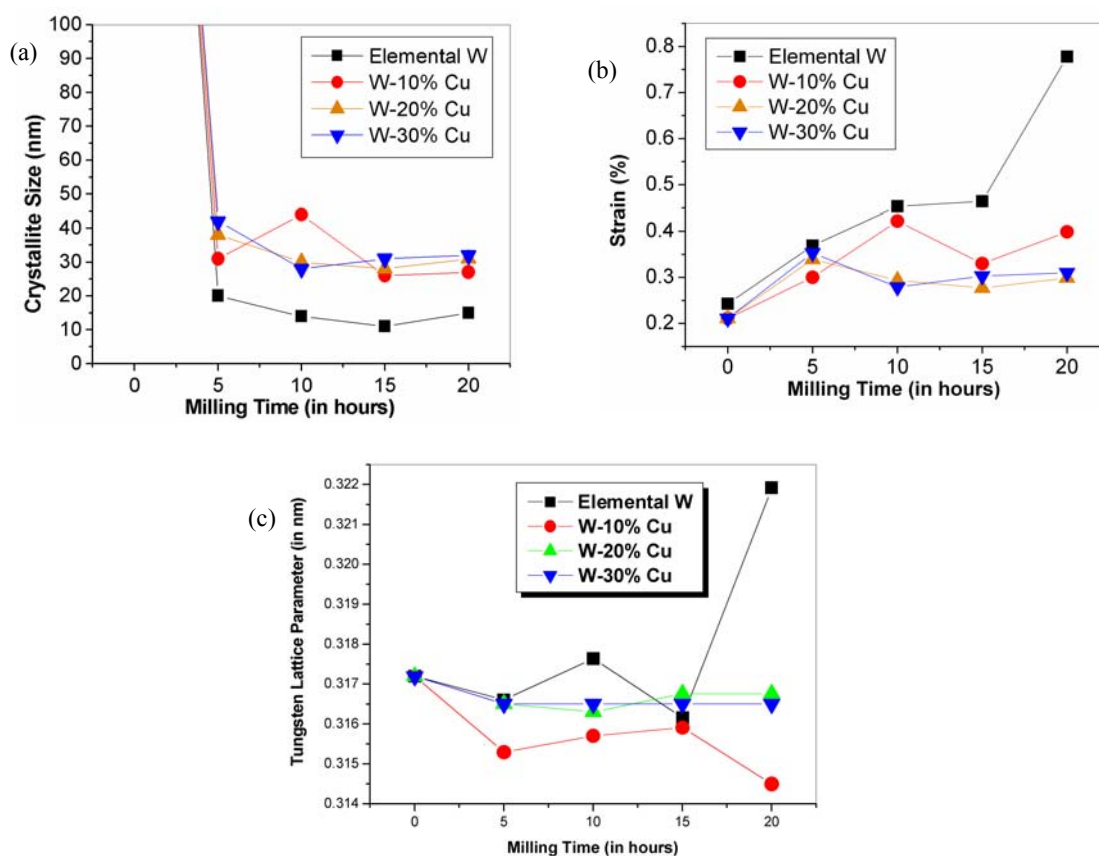


Fig. 2 Variation of (a) Crystallite Size (b) Strain (c) Lattice Parameter of W with milling time in W-10, 20, 30wt. % Cu.

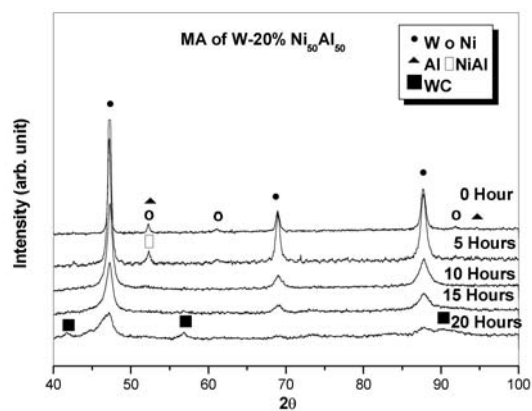


Fig. 3 XRD (Co K α) patterns of mechanically alloyed W- 20 wt.% Ni₅₀Al₅₀ as a function of milling time.

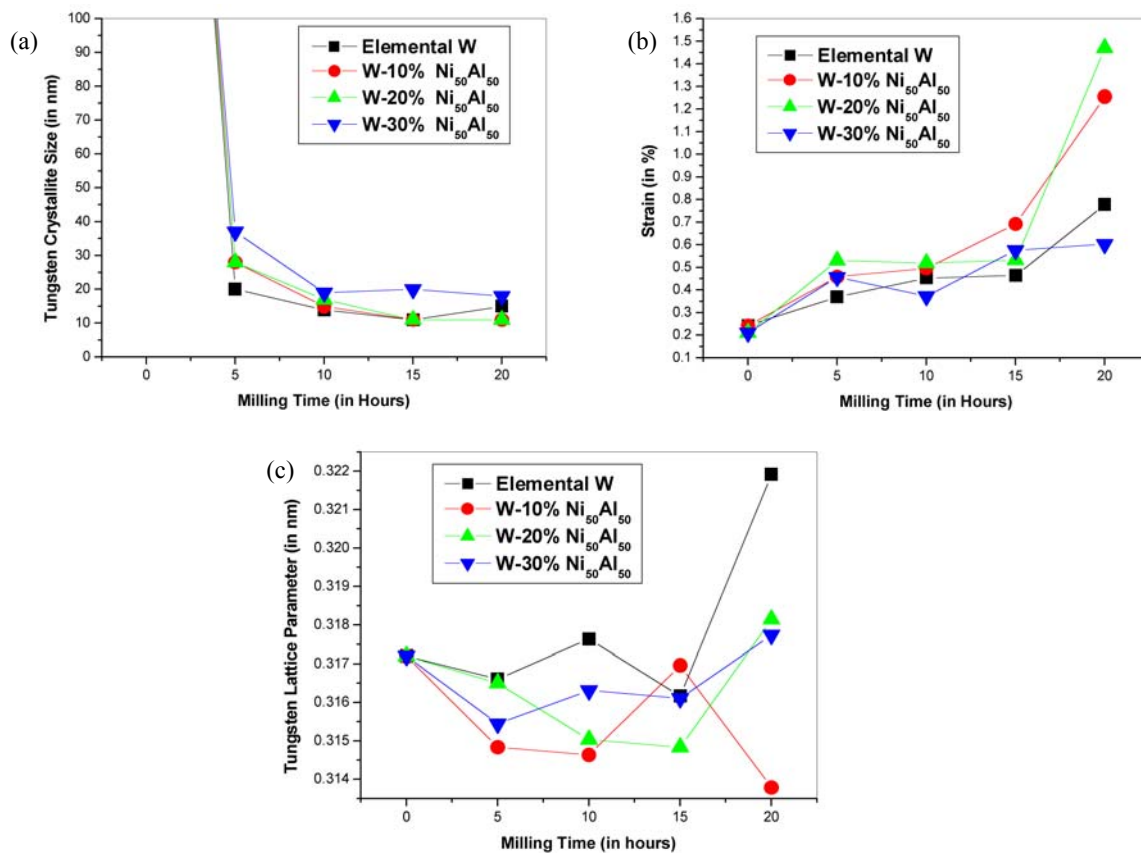


Fig. 4 Variation of (a) Crystallite Size (b) Strain (c) Lattice Parameter of W with milling time in W-10, 20, 30 wt. % Ni₅₀Al₅₀ system.

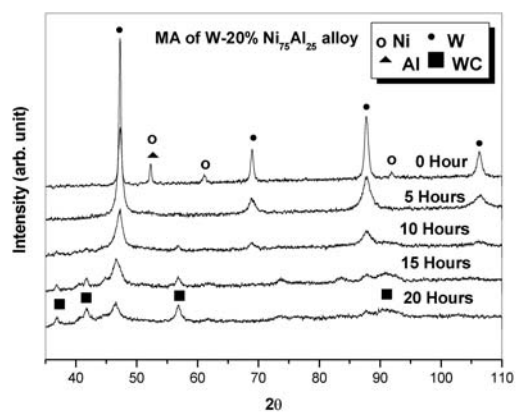


Fig. 5 XRD (Co K α) of mechanically alloyed W-20 wt.% Ni₇₅Al₂₅ as a function of milling time.

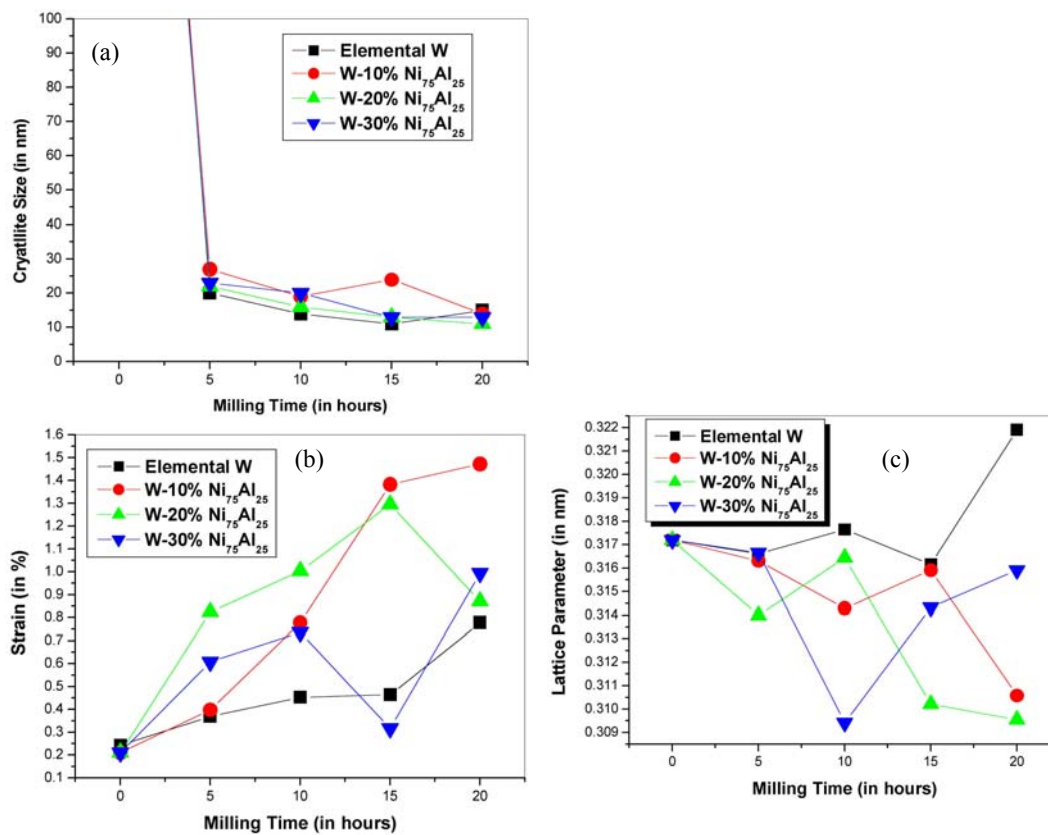


Fig. 6 Variation of (a) Crystallite size (b) Strain (c) Lattice Parameter of W with milling time in W-10, 20, 30 wt.% Ni₇₅Al₂₅ system.

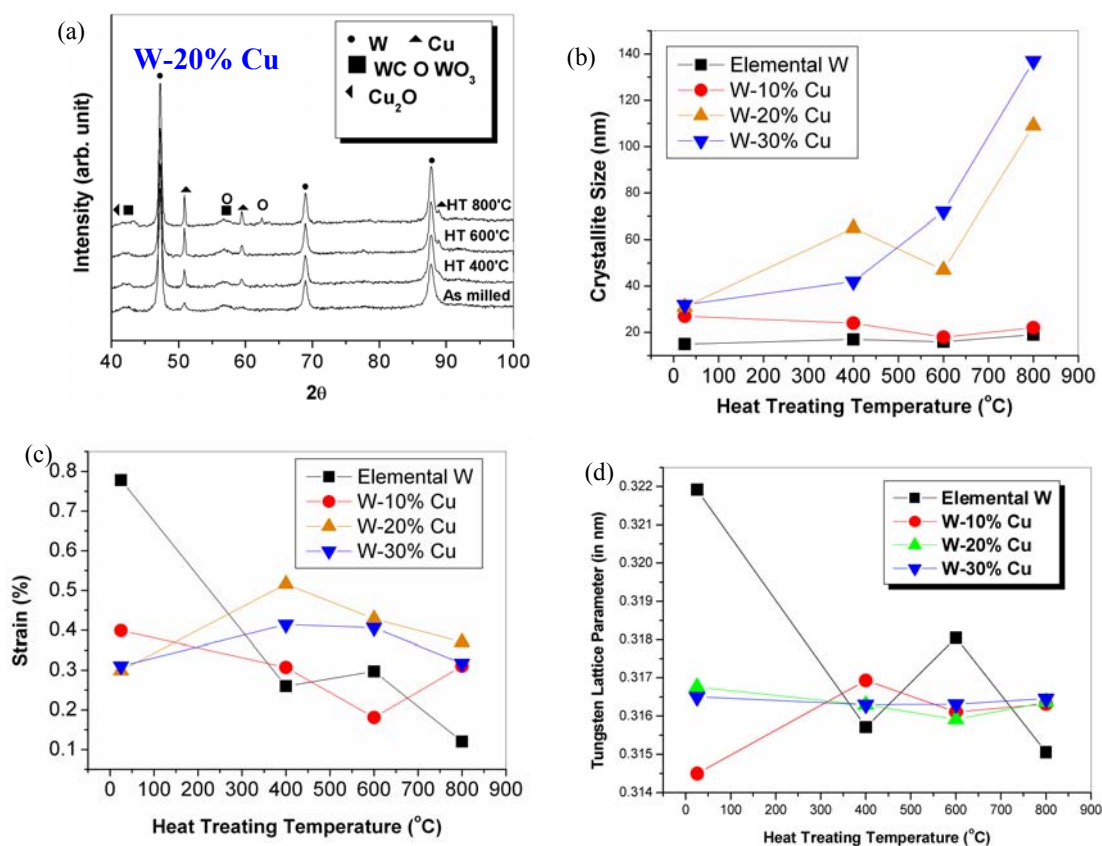
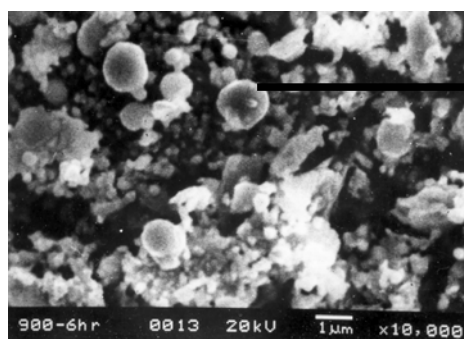


Fig. 8 (a) X-ray diffraction pattern of as-milled and heat-treated W-20wt.%Cu samples. The soaking time for all heat-treatments was 2 hours. X-ray target: $\text{CoK}\alpha$. Variation of (b) crystallite size (c) strain (d) lattice parameter of W with heat-treatment temperature in as-milled and heat-treated W-10, 20, 30wt.% Cu system.



	Element %	Atomic %
Cu	96.29	98.68
W	3.71	1.32

Fig. 9 SEM of W-20wt.% Cu – 20 hours MA sample compacted under 419MPa load and sintered at 900°C for 6 hours.

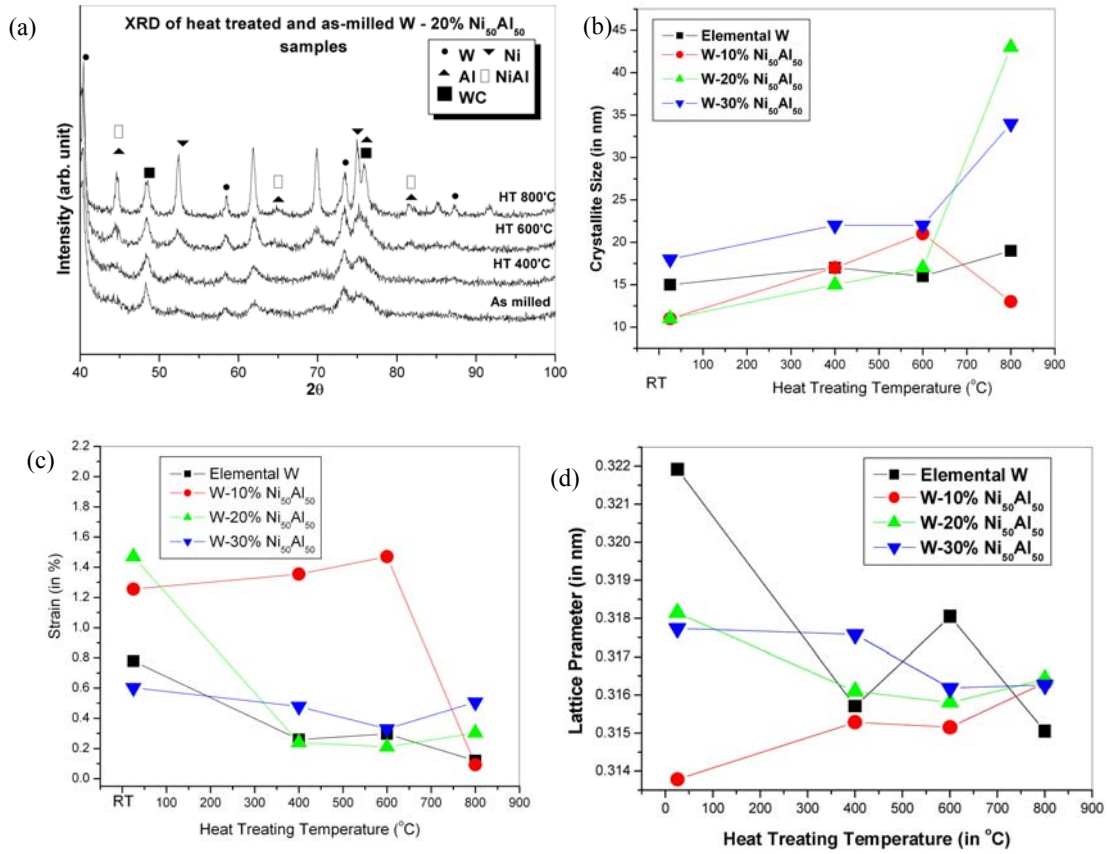


Fig.10 (a) X-ray diffraction pattern of as-milled and heat-treated W-20 wt.% Ni₅₀Al₅₀ milled for 20 hours. The soaking time for all heat-treatments was 2 hours. X-ray target: CuKα
Variation of (b) crystallite size (c) strain (d) lattice parameter of W with heat-treatment temperature in as-milled and heat-treated W-10, 20, 30wt.% Ni₅₀Al₅₀ system.

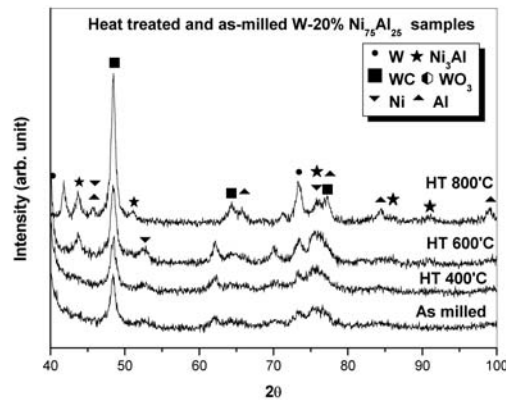


Fig. 11 X-ray diffraction pattern of as-milled and heat-treated W- 20 wt.% Ni₇₅Al₂₅ milled for 20 hours. The soaking time for all heat-treatments was 2 hours. X-ray target: CuKα

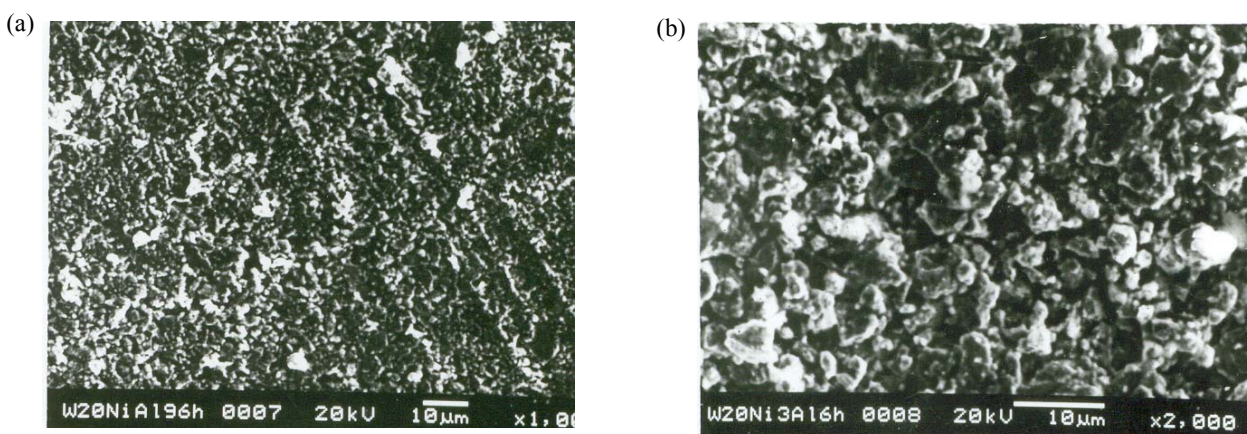


Fig.12 (a) SEM of W-20wt.%Ni₅₀Al₅₀ - 20 hours MA sample compacted under 419 MPa load and sintered at 900°C for 6 hours. (b) SEM of W-20wt.%Ni₇₅Al₂₅ - 20 hours MA sample compacted under 419 MPa load and sintered at 900°C for 6 hours