EFFECT OF BINDER COMPOSITION AND SINTERING TEMPERATURE ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF WC-7(Ni,Fe) HARD ALLOYS PREPARED BY FREE CAPSULE HIP TECHNIQUE

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Abstract
In this research, WC-7(Ni,Fe) hard alloys were prepared by ball milling, cold compaction and finally consolidated by hot isostatic pressing. The effect of binder composition and sintering temperature were investigated in term of the microstructure, density and mechanical properties of sintered samples. Density of hard alloys was measured by the Archimedes' principle while the microstructure was observed using a scanning electron microscope. The Vickers hardness was investigated at load of 30KG and the fracture toughness was calculated based on the Palmqvist crack method. The results revealed that the density of sintered samples was obtained in the range of 14.65 to 14.8 g/cm^3 meanwhile the measured Vicker hardness and fracture toughness were respectively achieved from 1260 to 1520 HV30 and 11,7 to 17,5 MPa.m$^{1/2}$ depending on the binder composition and sintered temperature.

Keywords: hard alloys, hot isostatic pressing, Vickers hardness, fracture toughness

1 Introduction

WC based hard alloys have been used in a wide range of applications including metal cutting tools, mining tools, wear resistant parts and wire-drawing dies [1-5]. Since the invention of WC hard alloys, Co metal has been the most optimum binder phase for producing these kinds of materials due to its good wettability to WC grains and high mechanical properties which bring to the remarkable properties of WC-Co hard alloys such as high hardness and toughness [5-8]. However, several drawbacks of using Co binder for WC hard alloys have been found such as low corrosion-, oxidation-resistance and the raising the suspects of harmful effects to human body concerning to WC-Co containing dust [3, 7-10]. Moreover, the high price and limitation of Co resource have to be taken into consideration. Recently, efforts have been paid to find out new binder alloys to replace Co in WC hard alloys in which Ni, Fe and their alloys have been considered as the ideal binders for WC hard alloys [2-7, 10-11]. The substitution of Co by Ni and Fe has been investigated in literature. The results showed that the Fe/Ni ratio plays an important role in the microstructure and properties of WC-Co-Fe-Ni hard alloys. The increase of Fe/Ni ratio would bring to the binder phase consisting of γ-(Fe,Ni), α-(Fe,Ni) or mixture of these two phases and subsequently, effected

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on the mechanical properties of WC-Co-Fe-Ni hard alloys [11]. The WC-Co-Fe-Ni hard alloys exhibited optimal properties when the binder phase was fcc structure [11-12]. The toughness of WC-(Fe,Ni) alloys could be improved using a suitable heat treatment and controlling the carbon content [13]. In addition, the corrosion resistance of WC-15(Fe,Ni) was considered to be better than WC-15Co alloy [14]. The results above show that Fe-Ni binder is considered to be a potential binder to replace Co for production of WC hard alloys. In this research, WC-7(Ni,Fe) alloys are fabricated using the hot isostatic pressing technique, an advanced technique to consolidate WC based hard metals [15-16]. The effect of Fe content and sintering temperature on the microstructure and mechanical properties will be brought out for discussions.

2 Experimental procedure

The raw powders used in this work were WC (< 3 µm, TaeguTec Co.), Ni (<5 µm, TaeguTec Co.) and Fe (<50 µm, Xilong scientific Co., Ltd.). The SEM images of raw powders are shown in **Fig. 1a,b,c**. The composition of hard alloys was designed for WC-7(Fe,Ni) in which Fe content was varied from 0 to 3 wt.%. The sample codes and composition are shown in **Table 1**. The hard alloy powders were produced by ball milling in n-hexane medium for 72 h using the WC-Co balls and jar. The ball to powder ratio was 6:1. The as-milled powders were then reduced in hydrogen gas flow for 4 h at 500 °C to eliminate the metal oxides formed during the ball milling. After the

Table 1 Sample composition of designed hard alloys

Sample code	WC-7Ni	WC-6Ni1Fe	WC-5.5Ni1.5Fe	WC-5Ni2Fe	WC-4.5Ni2.5Fe	WC-4Ni3Fe
Ni content (wt.%)	7	6	5.5	5	4.5	4
Fe content (wt.%)	0	1	1.5	2	2.5	3

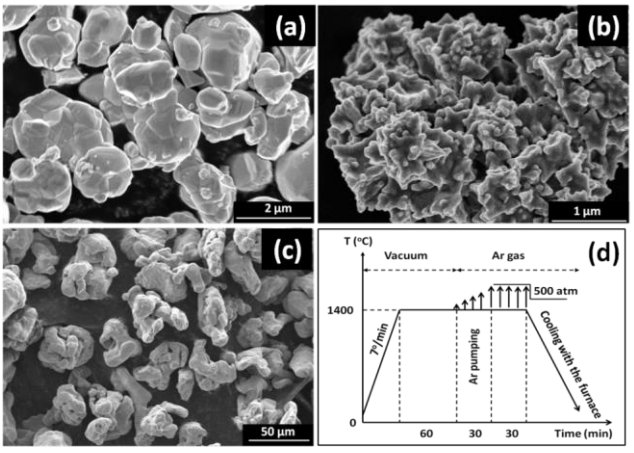

Fig. 1 SEM images of raw powders a)WC, b) Ni and d) Fe, and d) sintering scheme for samples.

hydrogen reduction process, the mixture powders were subsequently mixed with 2 wt.% paraffin wax as the pressing aid. The cold compaction was done in a cylindrical mould of 13 mm in diameter at the pressure of 1 ton.cm^{-2}. The obtained pellets were pre-heat treated at 800 ^{o}C for 1 h

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in Ar gas to eliminate the pressing aid and other organics contaminated in the samples. The pellets were sintered by free capsule hot isostatic pressing at different sintered temperatures. The sintering procedure was carried out as seen in **Fig. 1d** in which the samples were heated up to sintered temperature and kept at this temperature for 1 h in vacuum; the Ar gas was then pumped into the sample chamber to the pressure of 500 atm and held at this pressure for 30 min and subsequently, cooled to room temperature. The sintered samples were measured the density using Archimedes' principle. Phase component was analyzed by X-rays diffraction (XRD, Advanced Bruker, D5005) meanwhile the microstructure was observed using field emission scanning electron microscope (FE-SEM, Hitachi S4800). The mechanical properties were investigated in term of Vicker hardness, HV30 (Mitutoyo AVK-C0) and fracture toughness, K_{IC} based on Palmqvist crack method [17-19].

3 Results and discussion

3.1 The effect of Fe content

The effect of binder composition on the phase formation of samples sintered at 1400°C was analyzed based on the XRD patterns as shown in **Fig. 2**. In the sample without Fe (WC-7Ni), the main obtained phases are WC and Ni metal. When Ni was partially alternated by Fe, the results revealed the diffraction peaks of two phases; WC and γ-(Ni,Fe). Individual phases of Ni and Fe were not observed. This implied that the solid solution of NiFe was formed during sintering. Besides that the peaks of η-phase, $(W,Ni,Fe)_6C$, were not detected for all compositions, even with the sample containing 3 wt.% Fe. This assumes that the C content may be in the range of two-phase region [13, 20-21].

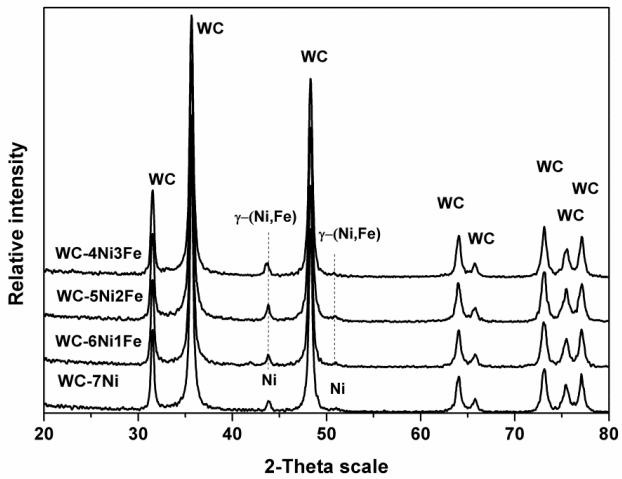

Fig. 2 XRD patterns of sintered samples with different composition.

Microstructure of sintered hard alloys was observed by FE-SEM equipment using back scattered electron mode as seen in **Fig. 3**. The bright colors, gray colors and black colors are WC, NiFe and micropores, respectively. The observed micropores in all specimens could be attributed to the insufficient sintered temperature and time or due to the low Ar gas pressure of HIP process. The measured densities of sintered samples are presented in **Fig. 4a**. It shows that the density of hard alloys decreased from 14.71 to 14.41 g/cm^3 as the amount of Fe increased from 0 to 3 wt.%. This

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is attributed to the lower density of Fe in comparison with the density of Ni metal. The appearance of pores leads to the decrease of the mechanical properties, especially for the toughness. The measured Vickers hardness and fracture toughness of sintered hard alloys are shown in the **Fig. 4b**. It is obviously to see the increase of Vickers hardness with the increase of Fe content. The Vickers hardness was about 1260 HV30 for the sample without Fe and then gradually increased to about 1520 HV30 for the sample using 3 wt.% Fe. Previous studies revealed that the hardness of hard alloys depend on the WC grain size, binder amount and binder structure. As the Fe content increased, the γ solid solution of Ni and Fe was changed and resulted in the increase of the hardness. The fracture toughness, however, has a trend to decrease with the increase of Fe content. The maximum value of K_{IC} was reached at 17.6 MPa.m$^{1/2}$ in the sample WC-7Ni and reduced to 11.7 MPa.m$^{1/2}$ in the WC-4Ni3Fe sample.

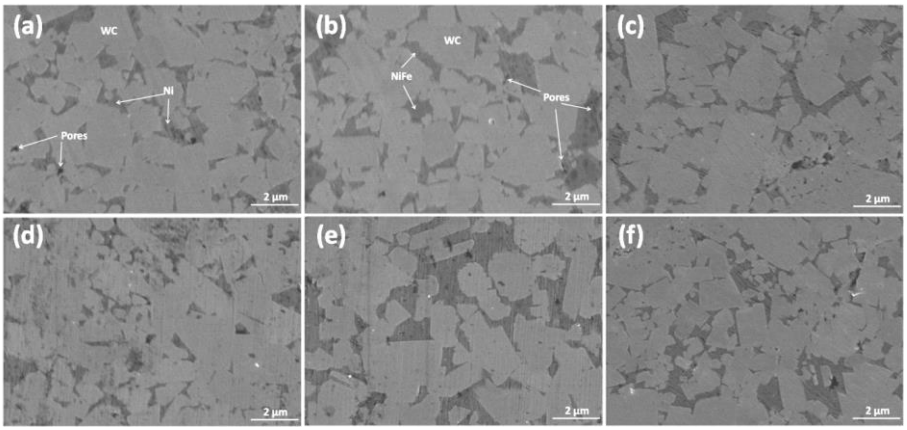

Fig. 3 FE-SEM images of; a) WC-7Ni, b) WC-6Ni1Fe, c) WC-5.5Ni-1.5Fe, d) WC-5Ni2Fe, e) WC-4.5Ni2.5Fe and f) WC-4Ni3Fe

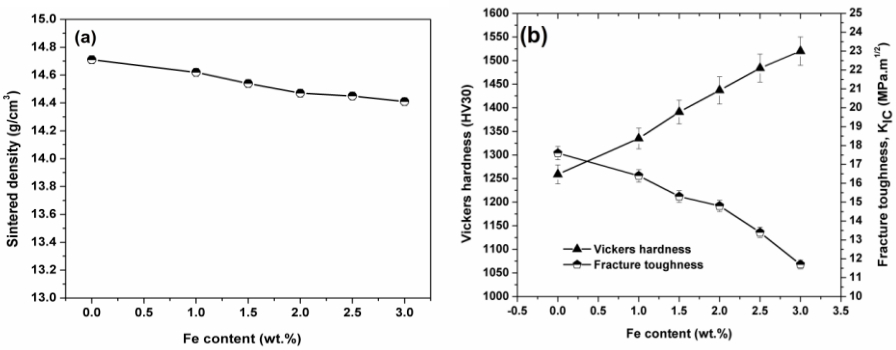

Fig. 4 Effect of Fe content on; a) density and b) mechanical properties of WC-7(Ni,Fe) alloys

3.2 Effect of sintering temperature

In order to investigate the effect of sintering temperature, the samples with composition of WC-6Ni1Fe were sintered at different temperatures; 1400, 1410, 1420 and 1440 °C using the same sintering schedule as presented in **Fig. 1d**. **Fig. 5** shows the XRD patterns of WC-6Ni1Fe hard alloys sintered at variety of temperatures. From **Fig. 5**, only diffraction peaks of WC and γ-(Ni,Fe)

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was observed in all samples, no η-phase or other phases was detected. The effect of sintering temperatures can be seen via the intensity of γ-(Ni,Fe) diffraction peaks. As the sintering temperature increased, the intensity of these peaks was greater which might be resulted from the growth of γ-(Ni,Fe) crystalline. **Fig. 6** shows the FE-SEM images of sintered samples. With the increase of temperature, the liquid phase of γ-(Ni,Fe) was more flexible to fill into the spaces between the WC particles and provided a higher driving force for consolidation of hard alloys during sintering. The FE-SEM images also show the grain growth and coarsening phenomenon of WC with the raising of sintered temperature. The density of sintered samples is presented in **Fig.7a**. A higher density was achieved at higher sintered temperature. The highest density was achieved at about 14.8 g/cm^3 for sample sintered at 1440 °C. It is close to the theoretical density calculated for WC-6Ni1Fe composition (14.813 g/cm^3). This shows that the HIP sintering technique can be used to consolidate these hard alloys to the full density.

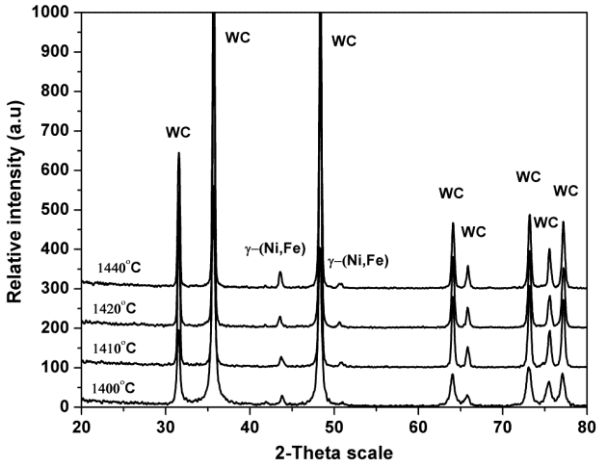

Fig. 5 XRD patterns of WC-6Ni1Fe sintered at different temperatures

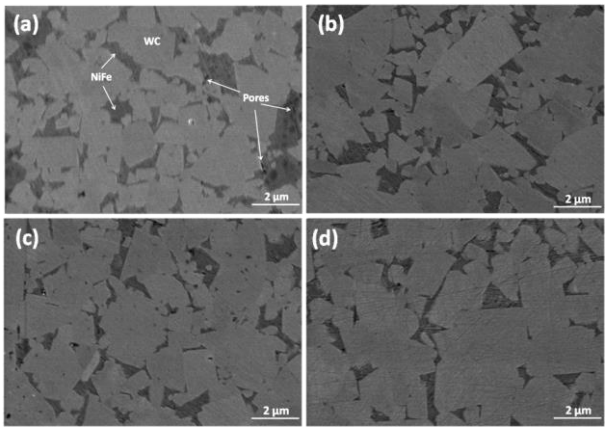

Fig. 6 FE-SEM images of WC-6Ni1Fe hard alloys sintered at; a)1400°C, b) 1410°C, c) 1420°C and d) 1440°C

Fig. 7b shows the effect of sintering temperature of the Vickers hardness and fracture toughness of WC-6Ni1Fe alloys. The Vicker hardness and fracture toughness increased from about 1335 to

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1378 HV30 and from 16.4 to 16.6 MPa.m$^{1/2}$, respectively, as temperature increased from 1400°C to 1410°C. And then, the hardness of alloys had a tendency to decrease whilst the fracture toughness continually increased to 17.1 MPa.m$^{1/2}$ with further increase of sintering temperature. The improvement of hardness of sample consolidated at 1410 °C was due to the higher density and the elimination of pores in the microstructure of hard alloy. Thereafter, the grain growth of WC was enhanced with the higher temperatures leading to the reduction of hardness following the Hall-Petch relationship [22-23]. The enhancement of fracture toughness was attributed to the better consolidation and grain growth of WC with the increase of sintering temperature.

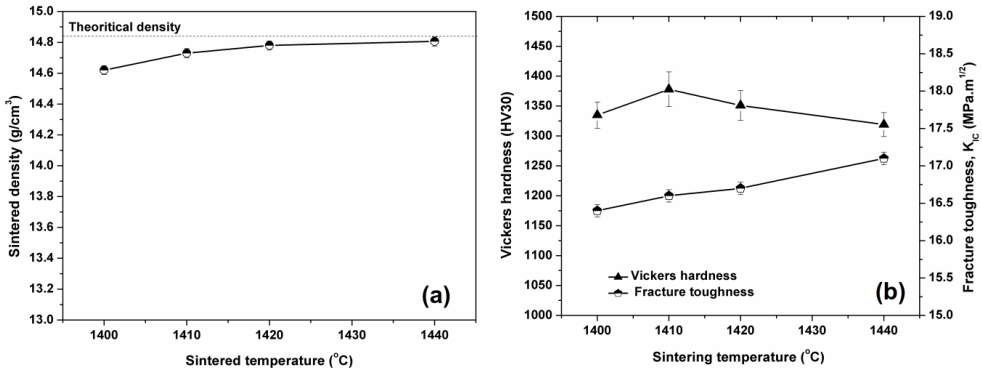

Fig. 7 Effect of sintering temperature on a) density and b) mechanical properties of WC-6Ni1Fe

4 Conclusion

In this work, WC-7(Ni,Fe) hard alloys have been fabricated via the powder metallurgy technology using hot isostatic pressing method. The results revealed that the mechanical properties of hard alloys strongly depended on the binder composition and sintering temperature. The replacement of Ni by Fe leaded to the improvement of hardness but also resulted in the reduction of fracture toughness. Increasing the sintering temperature leaded to the improvement of hard alloys' density and WC grain growth and therefore resulted in the enhancement of fracture toughness. The highest density and fracture toughness were reached at 14.8 g/cm^3 and 17.1 MPa.m$^{1/2}$, respectively, for the sample sintered at 1440 °C. However, the highest Vickers hardness value of 1378 HV30 was obtained for the sample sintered at 1410 °C and then, reduced with higher sintered temperature due to the grain growth of WC.

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