



## Preparation of W-Ni containing nano-composite powder using chemical co-precipitation route

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**Abstract:** Chemical coprecipitation route was applied for the system of W-Ni for the final goal of nano composite powder of WC-15%Ni. Nickel nitrate and sodium tungstate salts were used as Ni and W precursors respectively. Aqueous solutions of these salts were reacted under controlled pH condition prepared by ammonia addition and then the resulting precipitates were dried and calcined at 150°C and 450°C respectively. ICP, XRD, TGA and Scanning Electron Microscope were utilized for characterizing the samples. Using a basic medium with a pH of 12.50 which caused the formation of complex  $\text{Ni}(\text{NH}_3)_6^{2+}$  was found to provide suitable condition for precipitation of nanosized composite powders.  $\text{NiWO}_4$  and  $\text{WO}_3$  were the calcined produced powders. The chemical homogeneity of the calcined powders was observed by elemental map scanning. The nano size and the size uniformity of products were confirmed for as precipitated, dried and calcined powders.

**Keywords:** Chemical synthesis, Precipitation, Nanostructures, Composite materials

### Introduction

WC based cemented carbides have a leading position in industrial applications requiring good wear resistance, particularly abrasive wear resistance [1-2] like in the cutting-, drilling-, and forming-tool materials [3-4], because WC posses high hardness, a low coefficient of thermal expansion, a certain amount of plasticity, and good wettability by molten metal [2,5] and also the disadvantage of its brittleness is moderated by combining with metals (more ductile phases) like CO, Ni, Fe, etc [2]. Among them nickel has been used as the tough metal binder phase due to its excellent wetting, adhesion, and adequate mechanical properties. Nickel also has higher corrosion resistance than cobalt and thus has improved wear resistance in aggressive environments [1,2,4,6,7].

The common synthesis methods for WC-Ni cemented carbides use mechanical routes (powder metallurgy) to grind and homogenize the components [2,4,6,8-11] which have significant disadvantages of the high energy requirement and the loss of the fine grain structure and the pollution input as impurity from milling environment and tools [12-13]. Due to the density differences between WC and Ni, it is a challenge to mix them homogeneously by milling so it is difficult to have a uniform dispersion of size and uniform chemically distribution of components.

One of the newest methods used for this purpose is thermochemical process. Based on this method two different salt precursors are used to produce the precipitates substance and after the calcinations step a hydrogen reduction stage is made on the oxide powders in order to attain oxygen free bi-metal (in this case W-Ni) powders and then this composite powder should be carburized to get WC from elemental tungsten. Such a

route has been applied for the systems of W-Cu and W-Co successfully [12-15] due to the rich solution chemistry of tungsten (VI) which can form both stable and, due to slow kinetics, also metastable species and is known to polymerize and form several soluble polytungstate clusters [14]. By this method reaching to the goal of fine particle with high level of chemical and size dispersion is possible because of starting from a homogenous precursor containing ions of W and Ni mixed on the atomic scale. The precursor is converted to a uniform nanostructured WC-Ni powder by reduction and carburization.

Therefore, the goal of this study is to co-precipitate W-Ni sediments from their solutions and investigate results including the precipitation mechanism for the thermochemical co-precipitation of W-15%Ni nanocomposite based on the chemistry of coordination compounds, the morphology and chemical properties of products.

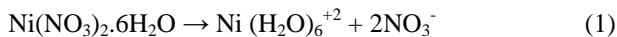
### Experimental

The precursors of W and Ni were aqueous solutions which were prepared by separately solving the proper salts,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , (>99.0% purity, Merck, Germany) and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99.0% purity, Merck, Germany) in the 200cc and 20 cc distilled water respectively. Concentration of Ni and W ions was based on the stoichiometric proportions to produce a final W-15wt%Ni powder. To adjust pH of the Ni solution on the base state (pH~12.50), ammonia solution was added. The two precursor solutions were mixed together and heated on a stirrer hot plate at 80-90°C for 4h in order to have desirable complexes precipitated. The precipitate was

separated from the solution by filtering and the remained solution was analyzed by ICP (Jobin Yvon 138) to check for any residual reactant elements. The Separated precipitates were washed several times and then heated at 140°C for 1.5h in the oven in order to dry (remove physical water). In order to determine the appropriate calcination temperature, the dried precipitates were subjected to thermogravimetry analysis (TGA) (Shimedzu TGA-50) up to 750°C with a heating rate of 10°C/min in air atmosphere. Then the dried powder was calcined in the electrical muffle furnace at 550°C for 2h and ambient atmosphere to have oxide powder. Calcined powder was analyzed by X-ray diffractometry (PW1800 Philips, Cu-K $\alpha$ ,  $\lambda=1.5406\text{\AA}$ ) to detect the produced phases. The microstructure and morphology of the powders and also their homogeneity were studied by scanning electron microscope (SEM, TESCAN model VEGA XMV) for as precipitated, dried and calcined powders. Tungsten and nickel distribution in the calcined samples were investigated by Elemental map scanning.

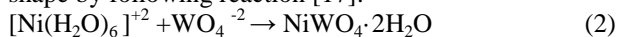
## Results and Discussion

The colour of the precursor salts of W and Ni were white and emerald green respectively. The nickel salt of  $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$  is solved in water by ionizing to ions of  $\text{Ni}^{+2}$  and  $\text{NO}_3^{-2}$  and the ion of nickel makes complex by accepting the  $\text{H}_2\text{O}$  molecules as in equation 1 [16]:

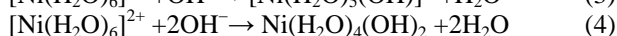
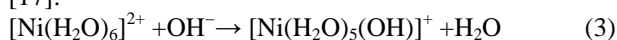


Nickel has an electron structure of  $\text{Ar}4s^23d^8$  and its electron structure of onion is  $\text{Ar}4s^03d^8$  so it has empty orbitals in 3d, 4s and 4p. Active lone pairs of electrons in the outer energy level of  $\text{H}_2\text{O}$  molecules are used to form co-ordinate bonds with the nickel ion as 6 ligands (lone pair donors) around  $\text{Ni}^{+2}$  (fig.1) molecules to form hydrolyzed nickel. This complex has light green colour. Tungsten salt solution is colourless and it has  $\text{Na}^{+1}$  and  $\text{WO}_3^{-2}$  ions, so it is alkaline as pH meter confirms (pH=9).

By mixing two solutions of Ni and W without adding  $\text{NH}_3$  to Ni solution, the sodden light green sediments were precipitate which were attached together with lump shape by following reaction [17]:



This is a simple replacement reaction which produces  $\text{NiWO}_4 \cdot 2\text{H}_2\text{O}$  precipitates which is not recommended due to large agglomerated precipitates it causes [17]. If ammonia addition is not sufficient the ions of  $\text{OH}^-$  which forms when  $\text{NH}_4^+$  takes hydrogen cation from water, react with Ni complexes. So following equations can occur [17]:



This can precipitate Ni in the molecule of  $\text{Ni}(\text{H}_2\text{O})_4(\text{OH})_2$  which has no bond with tungsten.

By adding ammonia solution gradually in the Ni solution its colour changed from light green to royal blue step by step. Ligand-exchange reactions of coordinated nickel complexes from  $\text{H}_2\text{O}$  to  $\text{NH}_3$  were happened through the following equation:



Worth mention it happens gradually by replacing the  $\text{H}_2\text{O}$  ligands with  $\text{NH}_3$  ones in the complex of Ni [16] and it changes the colour of the solution to royal blue. By adding a little amount of ammonia some precipitation appears and it turns to opaque turquoise, the related equation is 4 due to the  $\text{OH}^-$  ions of  $\text{NH}_3$  ionizing in water and therefore pH increasing in the solution. By more adding of ammonia in the solution the precipitates resolved back and the solutions became transparent violet blue through the equation 5 (fig.1).

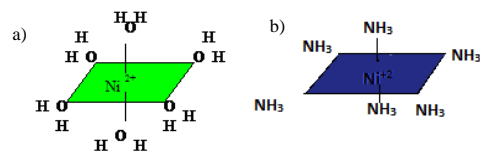
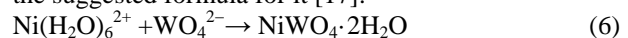


Fig.1- The complexes of  $\text{Ni}^{+2}$  with ligands of a)  $\text{H}_2\text{O}$  molecules and b)  $\text{NH}_3$  molecules.

The pH of the Ni solution after adding enough amounts of ammonia to get primary precipitates resolved was about 12.5. Then the solutions of nickel and tungsten were mixed together. The colour of the mixed solution remained violet blue and no precipitation happened immediately. By heating the mixture  $\text{NH}_3$  started to evaporate which was confirmed by testing by pH paper of the vapour. The precipitates formed by removing  $\text{NH}_3$  from the complexes and being replaced by  $\text{WO}_4^{-2}$  which also neutralized the charge and caused sedimentation. The colour of the solution after complete  $\text{NH}_3$  removal is light green and so are the precipitates. Equation 6 represents the suggested formula for it [17]:



Under mentioned conditions for this study the residual W and Ni in the remained solution after filtering the precipitates were analyzed by ICP which showed 1.83 and 0.27 ppm respectively. These amounts indicate that the thermochemical method has been successful in extracting W and Ni from their solutions.

After drying and calcination the physical and chemical  $\text{H}_2\text{O}$  can be removed.

TGA analysis results indicated 550°C as the proper temperature for calcination due to the cease of mass decreasing in the graph (fig. 2). The X-ray pattern of calcined sample confirms it in which the picks of  $\text{NiWO}_4$  and  $\text{WO}_3$  are presented (fig. 3). The Fig. 4 shows SEM images of as precipitated, dried and calcined samples. In the all images the particles are in the size range of ~30nm. And also an acceptable uniformity of size is observed in the pictures. The elemental maps of W and

Ni for calcined sample are demonstrated in the figure 5. It is obvious in these maps that a high uniform distribution of elements has been synthesized in calcined samples. It is a desirable accomplishment for the chemical precipitation method which was one of the main goals for this study.

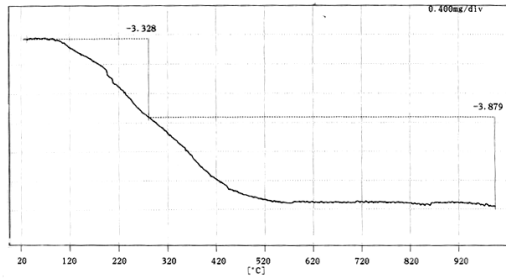


Fig. 2- TGA curve for the dried sample heated up to 750°C with a heating rate of 10°C/min in air atmosphere.

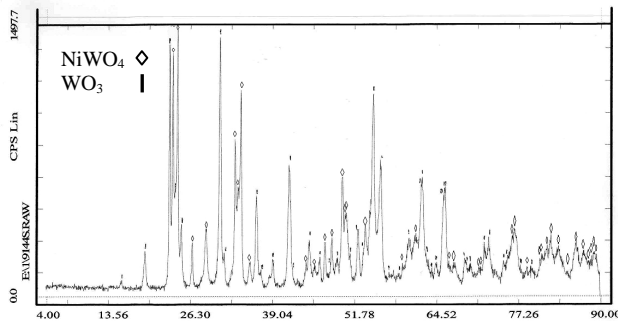


Fig.3 – X-ray pattern for calcined sample at the 550°C for 2h.

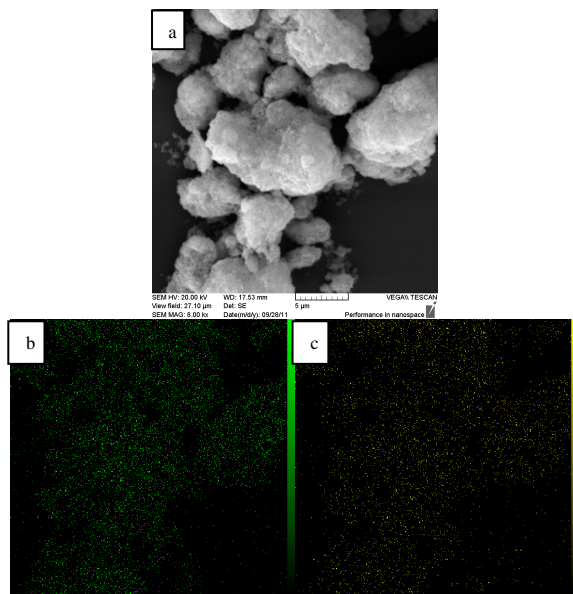


Fig. 4 – a) SEM micrograph of the calcined sample (WC-15%Ni), b) the Ni element map and c) W element map of the same sample.

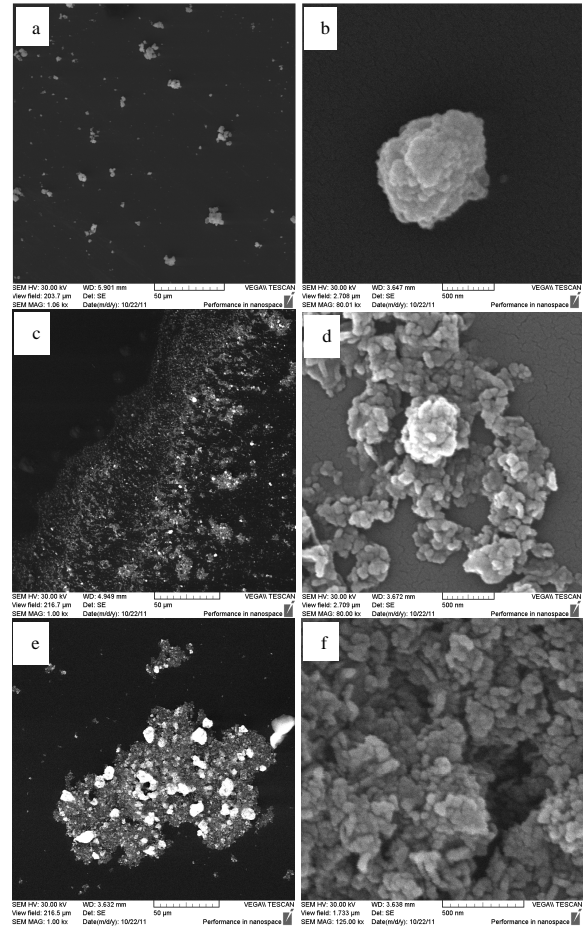


Fig.5 – SEM micrograph of a,b) as precipitated, c,d) dried and d,f) calcined samples in two magnification of 1000× and 8000×.

## Conclusions

In the system of W-Ni (for the final goal of WC-25%Ni), chemical coprecipitation was applied by using sodium tungstate and nickel nitrate as raw materials. The process includes precipitation of W-Cu compounds, drying and calcination of the initial precipitates in air. The adequate temperature for calcination was found 550°C. The results indicated an almost complete extraction of W and Ni from their solutions to the precipitate and also synthesis of nano structured powder after precipitation, drying and calcination. In addition an excellent uniformity in size and chemical distribution of the produced samples were obtained.

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