Effect of Temperature-Time on simultaneous hydrogen reduction of molybdenum and tungsten oxides

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Abstract

The Mo-30 wt% W solid solution is a well-established molybdenum-based alloy. A recent approach to alloying Mo and W involves the simultaneous reduction of their oxides by hydrogen. Several studies have reported the production of Mo-W alloys via the reduction of mixed oxides. But the alloying mechanism and the effects of key reduction parameters on alloy formation remain uninvestigated. In the present study, the simultaneous hydrogen reduction of MoO_3–WO_3 mixed oxides was investigated as a potential route for producing pre-alloyed Mo–W powders. In this study pre-alloyed Mo-30 wt% W is. The effects of reduction temperature and holding time on phase evolution, morphology, and alloy formation were systematically examined. The chosen temperature range is 600-1050°C. The influence of time on phase formation and morphology during the hydrogen reduction of molybdenum and tungsten oxides is examined over a 30-360 minute period. Other parameters such as heating rate ($20\frac{℃}{min}$), bed height (10mm), H_2 flow rate ($500\frac{ml}{min}$), and material weight (14.3g) were kept constant. The reduced samples are analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The effects of temperature and time on the reduction processes are closely linked. Results indicate the formation of MoO_2 and WO_2 phases at 600°C after 60 minutes of hydrogen reduction. No Oxide phases were detected in XRD analysis of the sample that was reduced at 800°C for 180 minutes. Therefore, tungsten and molybdenum coexist in all particles of the samples. Mass transfer between Mo and W takes place during the reduction of oxides to the metallic phase. But isothermal reduction does not yield a homogeneous alloy. In these studies, for T > 800°C, increasing time has minimal effect on alloying these elements. At T=800°C, a significant change in morphology occurs at t>180 min. At T=800°C, a notable morphological change occurs after t>180 min. These changes are caused by the CVT mechanism. The optimal conditions for achieving chemical homogeneity in the alloy powder particles after reduction were identified as: 600°C for 60 min, 600 to 1050 for 240 min, and 180 min at 1050°C. This cycle leads to the formation of homogeneous alloy powder particles. The achieved homogeneity is attributed to providing sufficient time for mass transport between molybdenum and tungsten oxide particles through gaseous chemical species formed within this temperature range.

Keywords: MoO_3–WO_3 mixture, hydrogen reduction, alloy formation, Temperature–Time effects.

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Introduction

Tungsten (T_m~3420ºC and ρ =19.2$\frac{g}{cm^3}$) and molybdenum (T_m~2620ºC and ρ =10.2$\frac{g}{cm^3}$) are refractory metals that exhibit outstanding properties at elevated temperatures [1,2]. These two metals show complete mutual solubility in both solid and liquid states [3]. Consequently, various molybdenum–tungsten alloys have been developed, among which Mo–30wt.% W is particularly well known. Mo-W alloys show higher strength at elevated temperatures compared to molybdenum and lower density relative to tungsten. Compared with pure molybdenum, Mo–30wt.% W alloy offers higher strength at elevated temperatures, while exhibiting lower density than pure tungsten. These alloys are commonly used in high-temperature components such as furnace heat shields and high-current electrical contactors. They are also employed in the zinc industry for the fabrication of molten zinc transfer pipes [3-6]. Mo-W alloys are typically manufactured using conventional powder metallurgy techniques, including elemental blending, mechanical alloying, and press sintering. Mo-W alloys are occasionally produced by vacuum melting processes [3,4,7&8]. In a study, tungsten and molybdenum metal powders were milled for 40 hours under an argon atmosphere. A ball-to-powder weight ratio (BPR) of 10:1 and a rotation speed of 200 rpm were selected for ball milling. It was claimed that In the XRD analysis, the main peaks corresponding to the individual phases of molybdenum and metallic tungsten were no longer observed. A homogeneous Mo-W alloy was obtained after heating the milling powders to 1600°C [6]. Producing pre-alloyed Mo–W powder directly during the oxide reduction stage eliminates the need for a separate alloying step, thereby product cost would be reduced. Accordingly, several investigations have focused on the synthesis of alloyed powders through the hydrogen reduction of molybdenum and tungsten oxides. As mentioned earlier, one of the most widely used tungsten–molybdenum alloys is Mo–30 wt.% W. Researchers have accordingly studied the production of pre-alloyed Mo–30 wt.% W powders via the simultaneous reduction of MoO_3 and WO_3. In a study, researchers used the aluminothermic reduction method. High-grade molybdenite (MoS_2) has been converted to MoO_3 by air roasting. Then, the MoO_3 was reduced by H_2 to MoO_2. Additionally, H_2WO_4 was heated in air to produce WO_3. The WO_3 was reduced to WO_2 using hydrogen. MoO_2, WO_2, an aluminum reductant, and a CaO flux were thoroughly mixed and then poured into the reactor cavity. The mixture was placed inside the reactor chamber. The reaction was finally initiated by bringing a freshly pickled burning magnesium ribbon in contact with the trigger mixture (potassium chlorate and aluminum taken in the ratio of 2:1 by weight). The CaO flux has

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been applied to the reduced metallic powder to facilitate the separation of the metallic powder from Al_2O_3. Subsequently, the reduced alloy powder was arc-remelted under argon atmosphere to produce a homogeneous alloy ingot of molybdenum and tungsten [9]. However, the reduction of tungsten and molybdenum oxides is predominantly carried out using hydrogen. In another study, a slurry of WO_3 and MoO_3 was prepared in camphene[1]. After spray drying, a porous solid comprising the two oxides was formed. Subsequent hydrogen reduction was performed at 900 °C for 1 h, followed by heat treatment at 1100 °C for 60 min under H_2 atmosphere, yielding Mo–30 wt.% W powder [10]. In a pre-alloyed powder, the homogeneous chemical composition of the entire powder is very important. One approach to achieving this homogeneity prior to the production of metal powder via reduction is to create powders of molybdenum and tungsten oxides with a homogeneous chemical composition. The formation of this homogeneous mixture by drying of a solution of molybdenum and tungsten oxides has also been investigated by researchers. In a study, highly soluble ammonium salts of tungsten and molybdenum were used to synthesize tungsten–molybdenum alloys. Spray drying of the ammonium tungsten–molybdenum solution at 140 °C produced a homogeneous mixture of the corresponding ammonium compounds. Then, the mixed oxides were reduced in an N_2/H_2 atmosphere with an H_2:N_2 volume ratio of 1:5 at 850 °C for 2 h and subsequently cooled under the same atmosphere. Finally, W–20, 40, 60, and 80 mol% Mo alloys were produced [11]. Also, researchers used the sol-gel method to obtain the Mo-W alloy. In this experiment, ammonium metatungstate and ammonium molybdate were used as metal compounds, while citric acid and ethylene glycol acted as complexing and polymerizing agents in the sol–gel process. The obtained gel was dried and calcined at 350–600 °C to remove organic compounds and form mixed oxide phases. Subsequently, the calcined powders were reduced in a hydrogen atmosphere at 600–900 °C. The results showed that calcination at 450 °C led to the formation of mixed oxides mainly consisting of $W_{0.4}Mo_{0.6}O_3$ and MoO_3, which were completely reduced to single-phase W–Mo solid-solution nanopowders at a relatively low temperature of 700 °C for 1 h [12]. However, in these studies, the effects of key parameters, including temperature, reduction time, and the characteristics of WO_3–MoO_3 powders, such as particle size and raw material purity, have not been systematically investigated. Moreover, no clear mechanism has been proposed for the alloying of molybdenum and tungsten during the reduction process. In the

1-Camphene is liquid at room temperature, and its chemical formula is $C_{10}H_{16}$.

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hydrogen reduction of MoO_3 and WO_3 (especially at T<600°C), volatile tungsten and molybdenum hydroxy phases can form, such as $WO_2(OH)_2$ and $MoO_2(OH)_2$. These volatile compounds originate from the reaction between water vapor and Mo and W oxides (especially WO_2 and MoO_2). These volatile compounds are reduced by hydrogen, and the reduced compounds precipitate on particles with lower oxygen content. This reduction process is known as CVT[1] [13-22]. These volatile compounds can facilitate mass transfer between tungsten and molybdenum during hydrogen reduction. In the hydrogen reduction of molybdenum oxide, another model is proposed to complete the CVT model, CCM[2]. Due to crystal changes and the formation of volatile compounds, cracks develop within the material. These cracks create pathways for hydrogen to enter and for volatile compounds to escape [16]. The CVT mechanism occurs at two stages of molybdenum and tungsten oxide reduction (MoO_3, WO_3 to MoO_2, WO_2 and MoO_2, WO_2 to Mo,W). Whereas CCM participates in the conversion of MoO_3 to MoO_2. CVT and consequently CCM mechanisms significantly influence grain morphology [13-17]. Considering the hydrogen reduction of both tungsten and molybdenum oxide is similar, and mass transfer by the CVT mechanism happens during the reduction process, it is necessary to investigate the effect of parameters on the formation of Mo-W alloy. Since hydrogen reduction is the most common method for producing tungsten and molybdenum metal powders, it is important to study the production of Mo-W alloy during hydrogen reduction. This study investigates the combined effect of temperature and time on the hydrogen reduction of mixed MoO_3-WO_3. How the two parameters influence alloy formation during oxide mixture reduction.

Raw materials and equipment

Materials

Commercial MoO_3 and WO_3 powders are available from Pars Molybdenum Company. XRF analysis is performed on MoO_3 and WO_3 to determine their purity. Table 1 presents the chemical analyses of the tungsten and molybdenum oxides used in this study. SEM image of MoO_3 and WO_3 Oxides after mixing is shown in Fig. 1.

1 - Chemical Vapor Transport

2 - Crackling Core Model

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Table 1- XRF analysis of MoO_3 and WO_3 used as raw material (All element quantities are reported in weight percent)

	MoO_3	WO_3	Fe_2O_3	NiO	CuO	SiO_2	CaO	Al_2O_3	L.O.I*	MgO	SO_3	Na_2O
Molybdenum Oxide	99.1	-	0.1	0.3	0.1	>0.01	>0.01	0.1	-	>0.01	>0.01	>0.01
Tungsten Oxide	-	99.2	>0.01	-	>0.01	>0.01	0.2	0.1	0.1	>0.01	>0.01	0.1

*** Loss on Ignition**

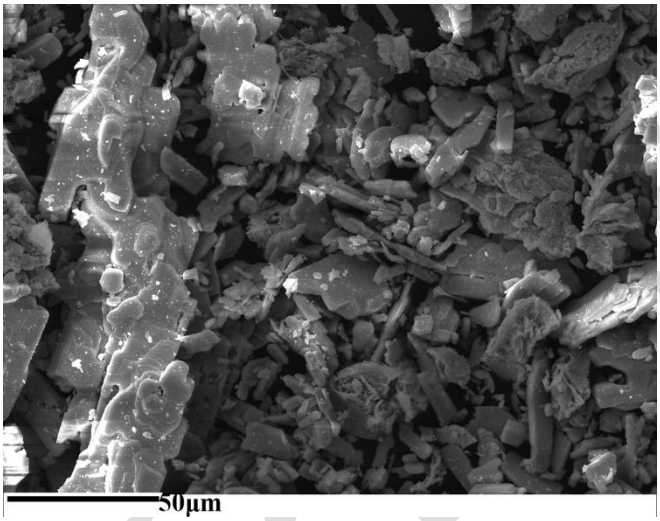

Figure 1- SEM image of MoO_3-26.5 wt.% mixture

Both tungsten oxide and molybdenum oxide are passed through 140-mesh sieves, resulting in particles smaller than 105µm. In this study, high-purity hydrogen and argon gas cylinders (<99.999%) were used as the reducing and protective gases, respectively.

Equipment

The main equipment used in this study is a tube furnace capable of reaching 1100°C. The furnace tube is made of stainless steel 310, and the boats are constructed from alumina. Additionally, a 140-mesh sieve and a balance with an accuracy of ±0.01g are used.

Analyzes

For elemental analysis, XRF (G.N.R Italy), for phase study, XRD (A.R.L USA), and for microscopic study, SEM (TECSCAN) have been used.

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Experiments

The main purpose of the experiments is to investigate the effects of time and temperature on the H_2 Reduction of tungsten and molybdenum oxides and their alloying during reduction. As mentioned earlier, the conversion of MoO_3 to MoO_2 is exothermic and may cause melting or evaporation due to MoO_3's low melting temperature ($T_m^{MoO_3} = 802℃$, $T_m^{MoO_2} = 1100℃$)[15&16]. Therefore, a step at 600 °C was included in the reduction cycle. For consistency in the experimental conditions, the 600 °C step was applied to all cycles (including tungsten oxide reduction). To obtain Mo-30wt.% W alloy, two oxides were mixed in a ratio that, after reduction, yields a molybdenum-to-tungsten ratio of 7:3. Therefore, 3.8g of WO_3 and 10.5g of MoO_3 were prepared for each test. The total mass of oxides and bed height of powder in the crucible were intended to be 14.3g and 10 mm, respectively, across all tests. In all tests, the hydrogen flow rate was $500\frac{ml}{min}$. To achieve the desired temperature more quickly, the heating rate was set to $20\frac{℃}{min}$. Initially, two separate oxide–reduction tests were designed to ensure the successful production of metal powder.

The separate reduction of these two oxides was studied at 1050°C for 90 and 180 minutes. The effect of temperature on Mo-W alloying was examined at 600, 700, 800, 900, and 1050°C. For the time study, a duration of 30-360 minutes was selected to examine the effect of time on alloying. Also, at 1050°C, a 480-minute cycle was tested to study diffusion during alloying. In all tests, after a specified reduction time, hydrogen gas input was stopped and replaced with inert gas (Ar) during cooling to prevent the cooling process from affecting the reduction. Table 2 shows hydrogen reduction cycles designed to examine the effect of time on Mo-W alloying.

Table 2- Reduction cycles of MoO_3-26.5% WO_3

T(ºC) / t(min)	600	700	800	900	1050
30	√	√	√	√	√
60	√	√	√	√	√
90	√	√	√	√	√
180	√	√	√	√	√
360	√	√	√	√	√
480	-	-	-	-	√

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After applying the mentioned cycles, the percentage weight loss of the samples was measured .All weight reductions presented are the average of two samples. The samples were analyzed by XRD to determine the phases formed. Then, EDAX analysis was used to examine the chemical composition of the powders and to observe phase formation. All experiments are schematically illustrated in Figure 2.

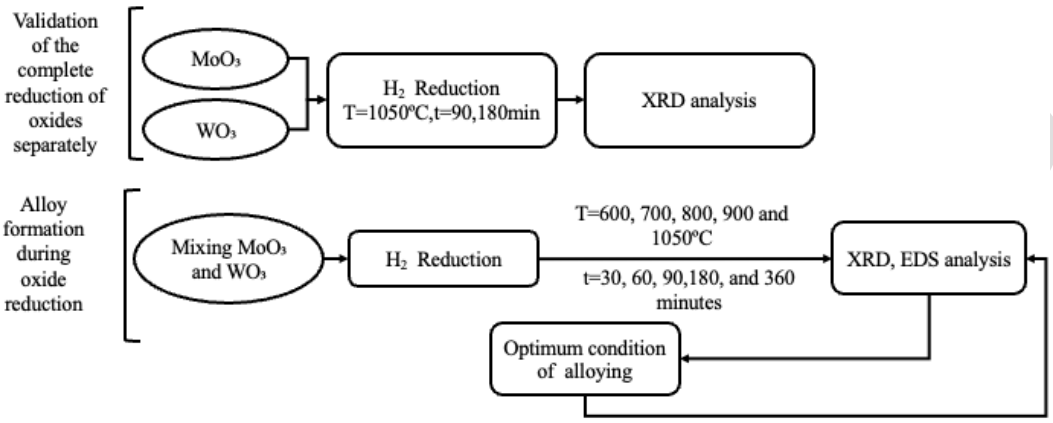

Fig 2- Flowchart of the experimental procedure

Results & Discussions

As previously mentioned, some tests have been conducted to evaluate the separate reduction of tungsten and molybdenum oxides. These tests have been designed to determine the reduction parameters at which tungsten and molybdenum oxides completely transform to metal. Table 3 shows the weight loss of MoO_3 and WO_3 after H_2 reduction at 1050°C for 90 and 180min. The theoretical values of oxide weight reduction are also presented in Table 3.

Table 3- Weight percent reduction of WO_3 and MoO_3 after separate reduction by hydrogen

Cycle	***MoO_3***	***WO_3***
600ºC,60min-1050ºC,90min (cycle 1)	33.4	20.7
600ºC,120min-1050ºC,180min (cycle 2)	34.5	21.28
Theory weight loss	33.3	20.9

As shown in Table 3 results, the reduction of hydrogen molybdenum oxides in terms of weight loss in cycle 1 (1050ºC, 90 min) is very close to the theoretical weight loss, and the weight loss of cycle is bigger than the theory. X-ray diffraction (XRD) analysis was performed on products of the reduction process of cycles 1 & 2. The results are shown in Figure 3. As shown in Figure 3,

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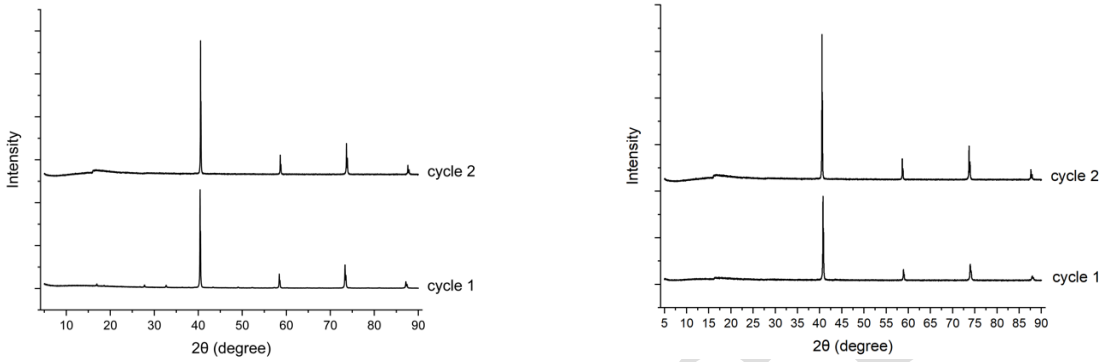
the XRD results for cycles 1 and 2 indicate that oxides are converted into single-phase Mo and W metal powders. Reduction of WO_3 in cycle 1 shows a slightly lower weight loss than theoretical. Increasing the time 90min to 180min (cycle 2) provides greater assurance of complete tungsten oxide reduction. Especially in reducing oxygen content in the metal powder during reduction [2].



(a) (b)

Figure 3- Comparison of X-ray Diffraction Pattern after Hydrogen Reduction in Cycles 1 and 2 (a) Tungsten (b) Molybdenum

Clearly, increasing time reduction leads to a greater decrease in oxygen. Therefore, as mentioned earlier, the cycle 2 time is used to study the effect of temperature on the simultaneous reduction of tungsten and molybdenum oxides. XRF analysis was performed to determine the chemical composition of reduced WO_3 and MoO_3 by cycle 2(Table 4).

Table 4- XRF analysis of products of H_2 reduction of MoO_3 and WO_3 (reduction condition: cycle 2)

Elements *	Mo	W	Fe	Ni	Cu	Si	Ca	Al	L.O.I	Mg	S	Na
W	-	99.5	0.1	0.1	0.1	<0.01	<0.01	0.1	-	<0.01	<0.01	<0.01
Mo	99.8	-	<0.01	<0.01	<0.01	<0.01	0.2	0.1	-	<0.01	<0.01	0.1

** All element quantities are reported in weight percent*

As shown in Table 4, the purity of metallic W and Mo is acceptable (with respect to the purity of oxides). As previously mentioned, to avoid the negative effects of released heat during the conversion of MoO_3 to MoO_2, a step at 600°C was considered. This step was considered in the separate reduction of oxides. In the reduction of the MoO_3-26.5wt% WO_3 mixture (to produce Mo-30wt% W after reduction), the impact of this step was examined. A powder mixture of oxides was reduced without being held at T=600°C in cycle 2 (Table 3). The weight loss was about 39.3%, which is undesirable, compared to the theoretical 30% weight loss. This excess of 9.3 wt.% weight

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loss disrupted the molybdenum-to-tungsten ratio. Therefore, in this reduction-cycle circumstance (especially at a heating rate of $20\frac{℃}{min}$), the heat generated during MoO_3 reduction causes the evaporation of oxides, especially molybdenum oxide. Consequently, stopping at 600°C is crucial to maintain the molybdenum-tungsten ratio. The weight-loss results from the mixed-oxide reduction are shown in Table 5. This test has been conducted to compare mixed and separate oxide reduction.

Table 5- Weight loss of MoO_3-WO_3 mixture after reduction over cycles 1 and 2 (C.V.[1]<1%)

Cycle type	Weight loss (%)
1	29.9
2	30.1
Theorical weigh loss	30

As shown in Table 5, the estimated weight loss closely matches the separate reduction and theoretical weight losses. In both cycles 1 and 2, the transformation of oxides to metallic Mo and W is nearly complete. Given that the oxides did not exhibit unusual weight loss in cycle 1, either during separate reduction or during reduction of the oxide mixture, the isothermal step at 600 °C was maintained at 60 minutes for the remaining reduction cycles. Based on the weight-loss data in Table 5, the weight loss of the mixed oxide samples at 180 minutes is more acceptable than at 90 minutes. These results are consistent with the findings from separate oxide reductions. Therefore, in cycle 2, the oxide mixture was completely reduced. Table 6 presents the weight-loss data for the MoO_3-26.5WO_3 mixture after hydrogen reduction at temperatures from 600-050°C for 30 to 480 minutes. As shown in Table 6, the weight losses of the reduced samples (the darker-shaded cells) closely match the theoretical values. So, these samples were converted to metal powder.

X-ray diffraction patterns of reduced MoO_3-26.5wt%WO_3 mixtures at $600℃ \leq T \leq 1050℃$ different times are presented in Figures 4-8.

To better understand the effect of time on the reduction of oxide mixtures, X-ray diffraction patterns are prepared for all samples. In Figure 4, XRD results of the reduced oxides mixture at 600℃ (30-360min) are presented

1 -Coefficient of Variation

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Table 6– weight reduction percentages of MoO_3-26.5WO_3 at different times at 600-1050°C

T(°C) / t(min)	600	700	800	900	1050
30	11.0	15.5	17.3	29.5	29.8
60	11.2	18.4	18.6	31.4	31.3
90	12.3	24.5	29.7	31.0	31.8
180	15.6	25.7	30.7	30.9	31.1
360	15.2	30.3	29.9	33.0	31.9
480	-	-	-	-	32.8

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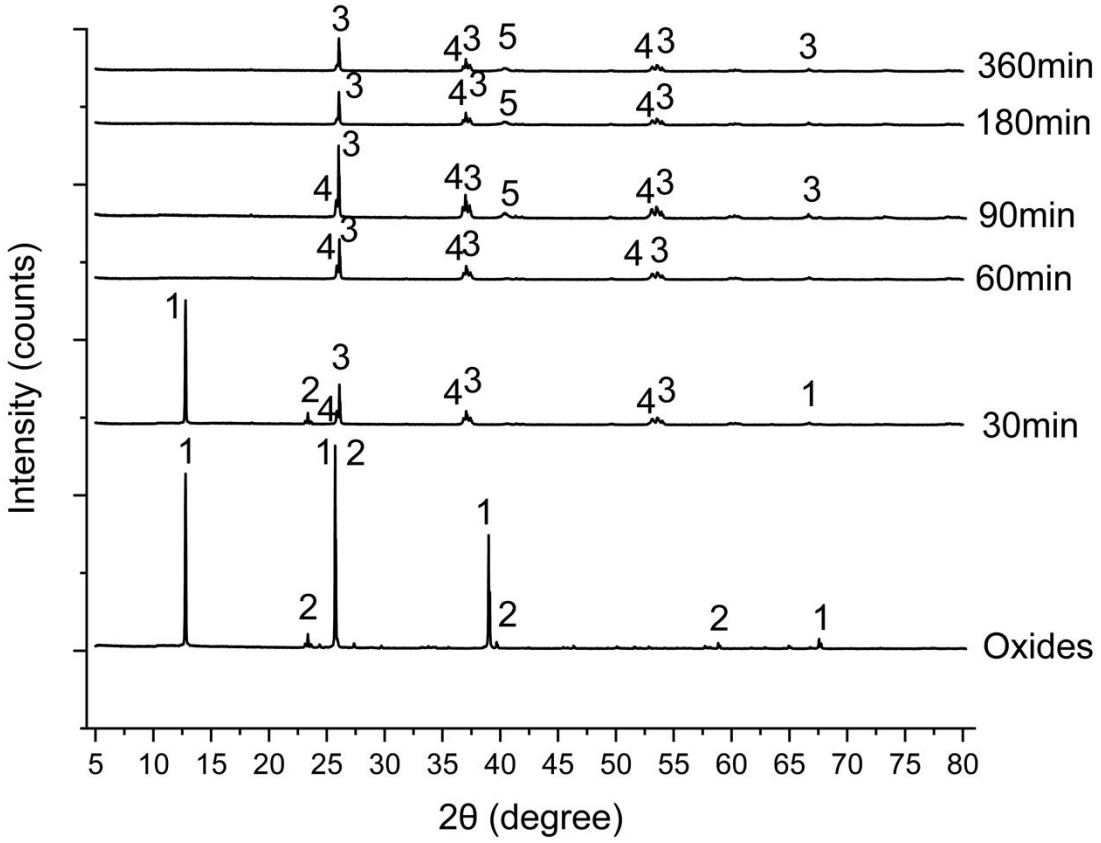

Figure 4- XRD results of reduced MoO_3-26.5WO_3 at 600°C at different times (1:MoO_3, 2:WO_3, 3:MoO_2, 4:WO_2, 5:Mo, 6:W)

As shown in Figure 4, at T=600°C, MoO_3 and WO_3 remain present after 30 minutes. However, after 60 minutes, all trioxide phases convert to dioxides (MoO_2 and WO_2). This evidence shows

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that the step at 600ºC for 60min is sufficient to convert MoO_3 to MoO_2. MoO_2 and WO_2 phases remain stable under these conditions for up to 360 minutes. The phase analysis results are in good agreement with the samples' weight loss. The metallic phase of molybdenum appears after 90 minutes of reduction at 600°C. However, even with an extended reduction time up to 360 minutes, its intensity does not change significantly, and MoO_2 and WO_2 phases are always observed alongside it. This indicates that, at 600°C, the conversion of molybdenum and tungsten dioxides to metallic phases is slow and requires a prolonged period. Figure 5 displays the X-ray diffraction patterns of MoO_3-26.5wt.% WO_3 reduced by H_2 at 700°C for 30-360 minutes. As shown, reducing the oxides mixture at 700°C for 30 minutes results in the formation of MoO_2 and WO_2 phases. However, some of the initial phases of MoO_3 and WO_3 have remained. With an increased cycle time to 60 minutes, the trioxide phases disappear and transform to dioxides. This dioxide stability persists until 360 minutes at 700 °C. However, from 90 to 360 minutes, the intensity of the dioxide phases decreases, while the intensity of the metallic phase increases. The metallic phase is detectable at 700°C after 30 minutes, but complete conversion of all oxides to the metallic phase does not occur after 360 minutes. Another notable feature of the X-ray diffraction pattern in Fig. 5 is the metallic character of the peaks. For $t \leq 180$ minutes, in the 2θ of the peaks corresponding to the metallic molybdenum (or tungsten) phase, rather than a single sharp peak, two closely spaced peaks are observed. Because the X-ray diffraction patterns of tungsten and molybdenum are similar. So, this suggests the coexistence of two phases with similar peak positions. Although at t=360 minutes the metallic phase peaks remained broad, at $2\theta=40°$ the diffraction peak sharpened and shifted toward a single-phase state, possibly indicating that some tungsten dissolved into molybdenum. However, a more precise assessment will be conducted during the EDAX analysis. In Figure 6, the results of the phase Analysis of MoO_3-26.5 wt.% WO_3 reduced by H_2 at 800°C for 30-360 minutes are shown. The effect of time at 800°C on the reduction process is similar to that at 700°C. The only difference is that the oxide phases ultimately disappear completely. As shown in Figure 7, heating at 800°C for 30 minutes causes the molybdenum trioxide and tungsten trioxide phases to vanish and convert into the dioxide phase.

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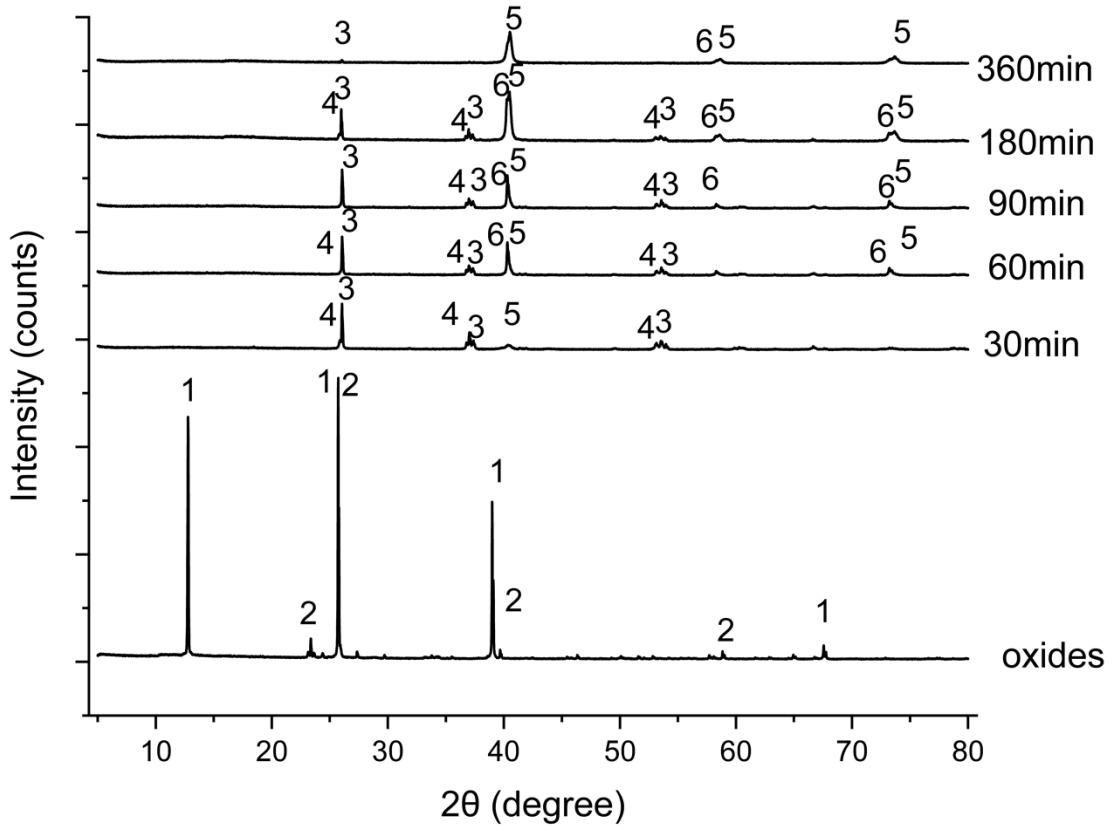

Figure 7- XRD results of reduced MoO_3-26.5WO_3 at 700°C at different times (1:MoO_3, 2:WO_3, 3:MoO_2, 4:WO_2, 5:Mo, 6:W)

Even at t=30 minutes, the metallic phase of molybdenum is visible. The reduction of tungsten and molybdenum oxide phases continues until 180 minutes, after which the oxide phases completely disappear. In the reduced sample at 800ºC for 360 minutes, two peaks remain obviously different, whereas at 360 minutes at 700ºC, the X-ray diffraction pattern is closer to single phase. This point is worth considering when achieving a homogeneous alloy, as increasing the temperature has not helped form one. Further investigations on the reduced samples will be conducted using SEM images.

The main difference between these two temperatures is the rate of oxide reduction, which is generally higher at 800 °C because oxides disappear more quickly. This can hinder the formation of a uniform alloy because the rapid formation of the metallic phase in the system hinders mass transfer toward volatile compounds. Then, alloy formation must proceed via diffusion within the metallic phase. Given the high melting points of molybdenum and tungsten, 800 °C is relatively low for effective diffusion of tungsten or molybdenum atoms.

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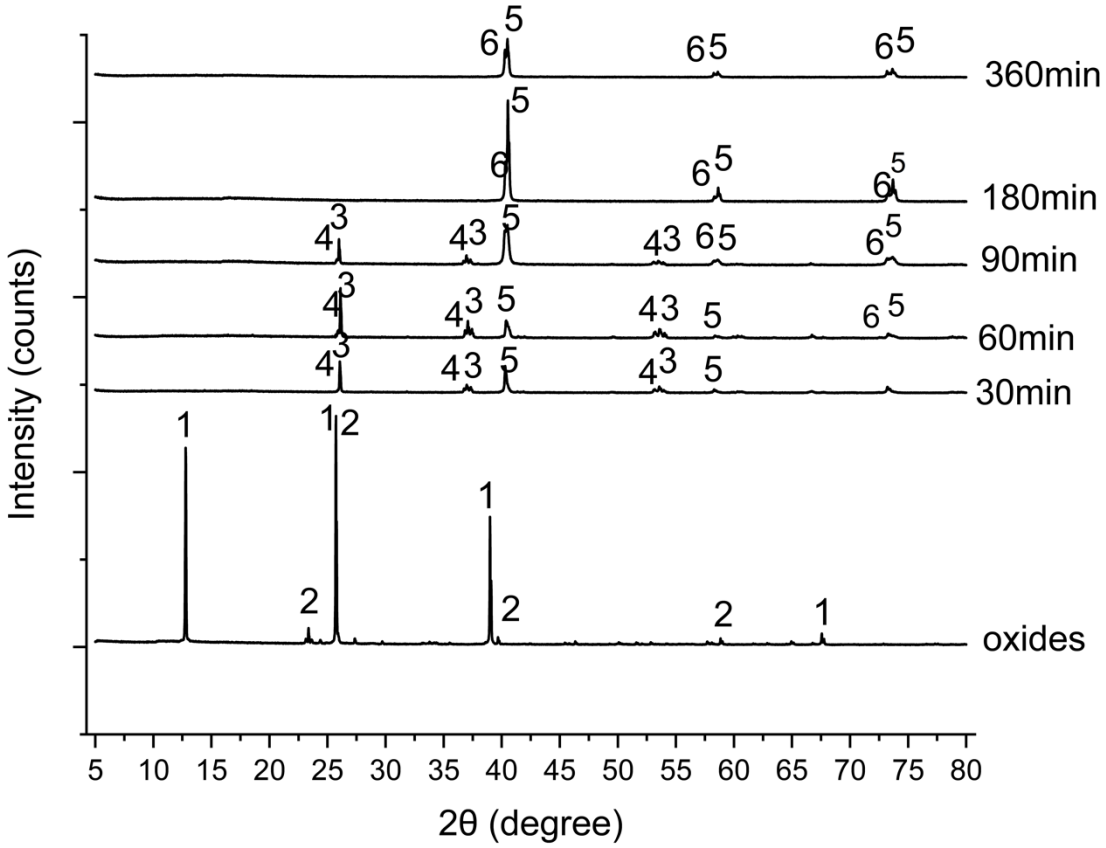

Figure 6- XRD results of reduced MoO_3-26.5WO_3 at 800°C at different times (1:MoO_3, 2:WO_3, 3:MoO_2, 4:WO_2, 5:Mo, 6:W)

Figures 7 and 8 display the X-ray diffraction patterns of mixed molybdenum and tungsten oxides reduced at 900°C and 1050°C under a hydrogen gas flow.

The behavior of oxides during hydrogen reduction at 900°C and 1050°C is similar. At both temperatures, after 30 minutes of H_2 reduction, only small amounts of MoO_2 and WO_2 remain. However, at 1050°C, the peak intensities of the oxide phases are significantly lower than at 900°C. After 60 minutes of reduction at these temperatures, the peaks of the oxide phases completely disappear. This indicates that the hydrogen reduction rate of tungsten and molybdenum oxides increases with temperature.

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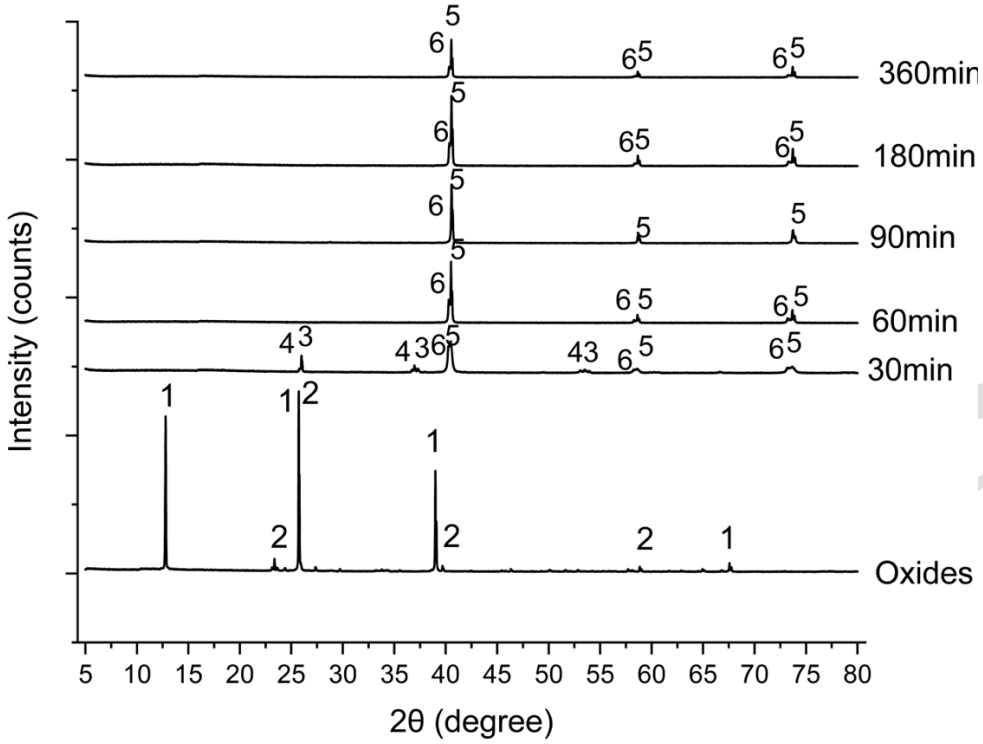

Figure 7- XRD results of reduced MoO_3-26.5WO_3 at 900°C at different times (1:MoO_3, 2:WO_3, 3:MoO_2, 4:WO_2, 5:Mo, 6:W)

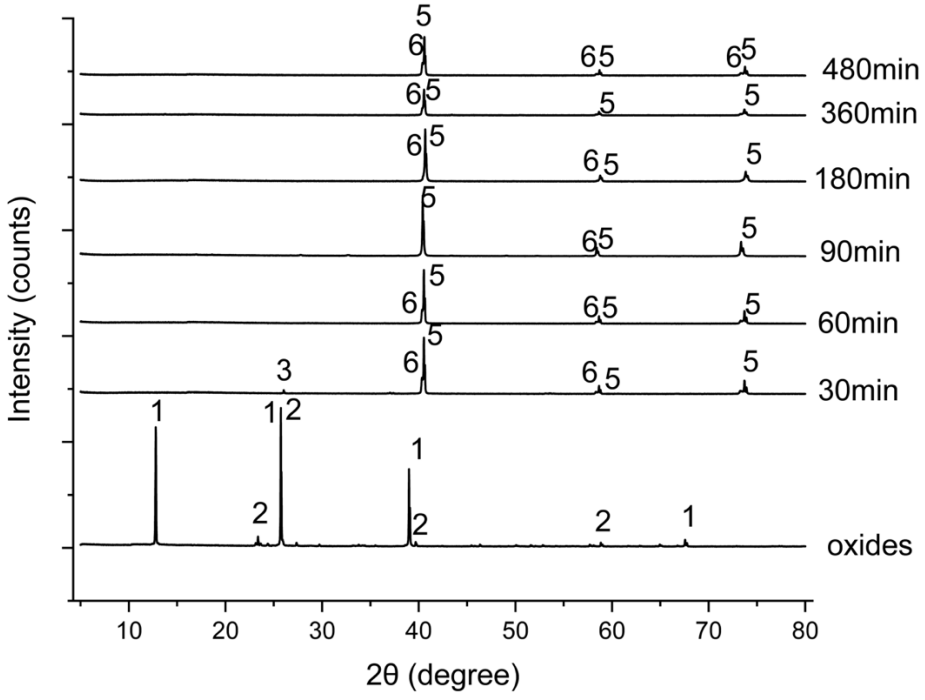

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Figure 8- XRD results of reduced MoO_3-26.5WO_3 at 1050℃ at different times (1:MoO_3, 2:WO_3, 3:MoO_2, 4:WO_2, 5:Mo, 6:W)

However, at 900°C and 1050°C (as at T=800°C), an additional tungsten-related peak remains at the same position as the molybdenum peaks (even after 360 minutes reduction). A reduction test was conducted at 1050°C for 480 minutes to investigate the effect of increasing time at maximum temperature on alloy formation. However, no significant change was observed in the phase pattern. Since oxide phases are practically no longer observed after 60 minutes at 1050°C, a diffusion-driven process will promote the formation of a solid solution. However, as observed, even after 480 minutes, a single-phase solid solution has not yet formed. This is similar to 800°C and 900°C, where increasing the time does not affect the formation of a single phase. At 900°C and 1050°C, the reduction rate increases, leading to the reduction of oxide phases and preventing the formation of volatile phases needed for mass transport. Therefore, Mo and W must diffuse to form an alloy, but the temperature is too low for efficient diffusion. Even after 480 minutes of reduction at 1050°C, the XRD pattern remains largely unchanged relative to that after 60 minutes. Figure 9 compares the effect of temperature at 180 minutes on the formed phases. At 180 minutes, the oxide weight loss during reduction has remained almost unchanged.

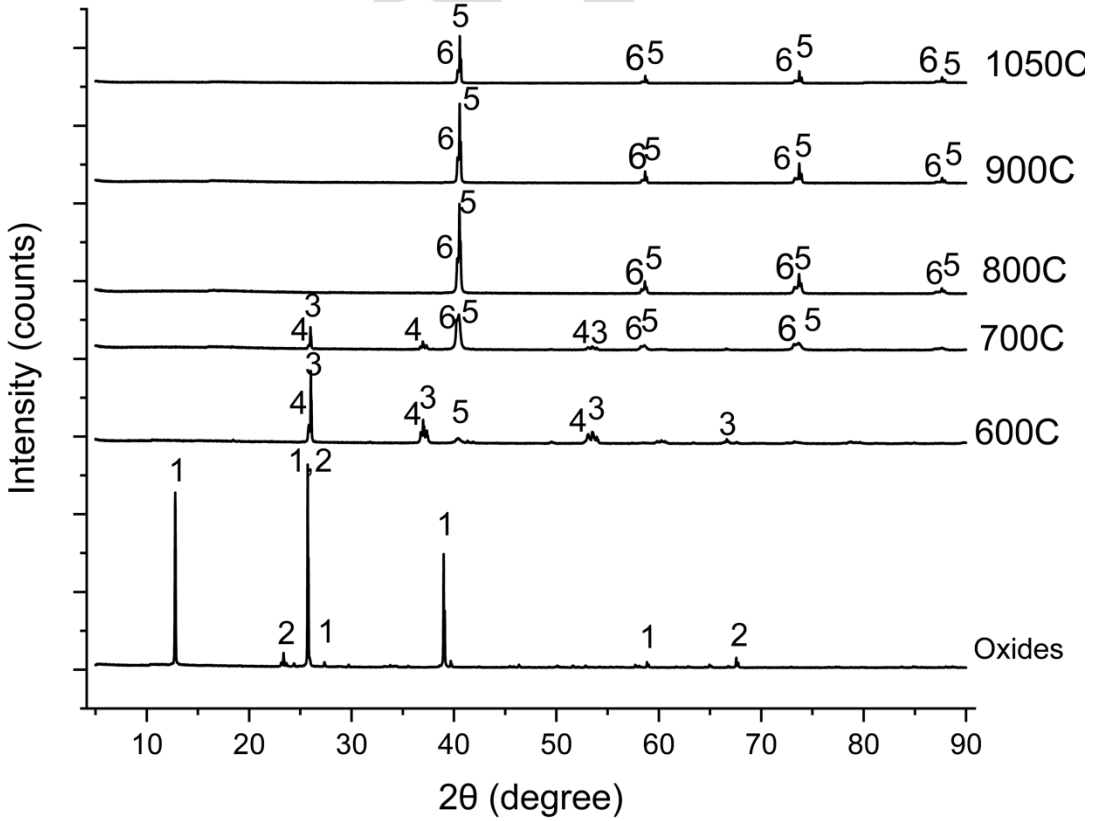

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Figure 9- The effect of temperature on the X-ray diffraction pattern of the product of the hydrogen reduction process of the mixture of molybdenum and tungsten oxides in order to produce Mo-30wt% W alloy (1:MoO_3, 2:WO_3, 3:MoO_2, 4:WO_2, 5:Mo, 6:W)

As shown in Fig. 9, heating to 600 °C eliminated the MoO_3 and WO_3 peaks present in the MoO_3–26.5 wt.% WO_3 mixture, and MoO_2 and WO_2 phases were observed. The formation of molybdenum dioxide at 600 °C prevented material loss during reduction because the melting point of the molybdenum oxide phase increased from approximately 800 to 1100 °C. Increasing the reduction temperature to 700 °C produced mainly MoO_2 and WO_2 peaks, together with weak peaks corresponding to metallic molybdenum and tungsten. At 800 °C, consistent with the measured weight loss of 30.7%, only metallic molybdenum and tungsten phases were detected, indicating complete reduction after 180 min. Further increasing the temperature to 900 and 1050 °C did not eliminate the distinguishable tungsten peaks adjacent to the molybdenum peaks. These changes were further examined by SEM and EDAX. Although EDAX is not highly accurate for quantitative oxygen analysis, it is useful for identifying trends in chemical composition with temperature. Figures 10–14 present SEM/EDAX analyses of MoO_3–26.5 wt.% WO_3 samples reduced at 600–1050 °C for selected times of 30, 180, and 360 min. In interpreting these analyses, it should be noted that chemical variations at different points are associated with the phases present in those regions.

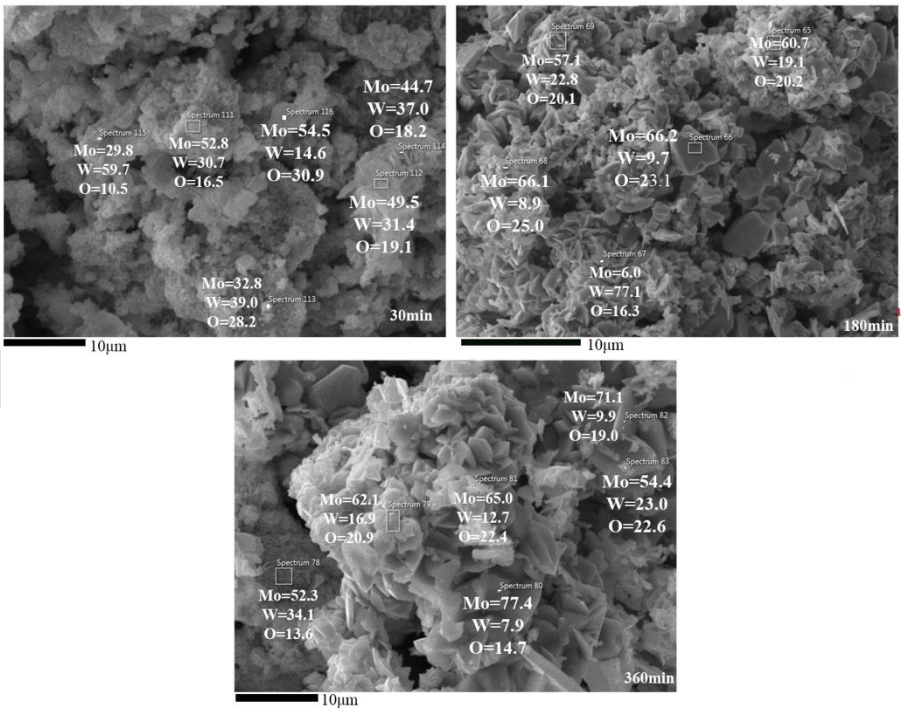

Fig 10- EDAX analysis of the reduced sample MoO_3-26.5wt% WO_3 at 600°C

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For example, in regions with higher molybdenum content, molybdenum-rich phases dominate. Considering that the molybdenum phases identified in the XRD analysis are Mo, MoO_3, and MoO_2, and based on the oxygen content, it is possible to determine which molybdenum phases are present at specific points. The tungsten phases analyzed by XRD include WO_3, WO_2, and W. If molybdenum and tungsten are often found together, a mixture of tungsten and molybdenum phases exists. Therefore, where MoO_3 and WO_3 are present, roughly 30 wt% oxygen will be observed on a macroscopic scale. On a microscopic scale, the MoO_3 particles contain about 33.3 wt%, and the WO_3 phase ~21 wt%. In other areas, depending on the phase percentages, the oxygen content varies between 33.3 and 21 wt.%. Of course, the error in EDAX analysis—especially for oxygen—must be considered. Figure 10 shows the EDAX analysis of the mixed-oxide sample reduced at 600°C. As shown in Fig. 10, a significant amount of oxygen remains even after 360 minutes of H_2 reduction. This observation aligns with the XRD phase analysis, which indicates that after 360 minutes of oxide reduction at 600°C, the predominant phases are MoO_2 and WO_2.

At T=700°C (Fig. 11), although the amount of oxygen decreases over time, a significant amount of oxygen remains even after 360 minutes. For comparison, the EDAX analysis of the oxide powder mixture MoO_3-26.5wt% WO_3 is shown in Fig. 15.

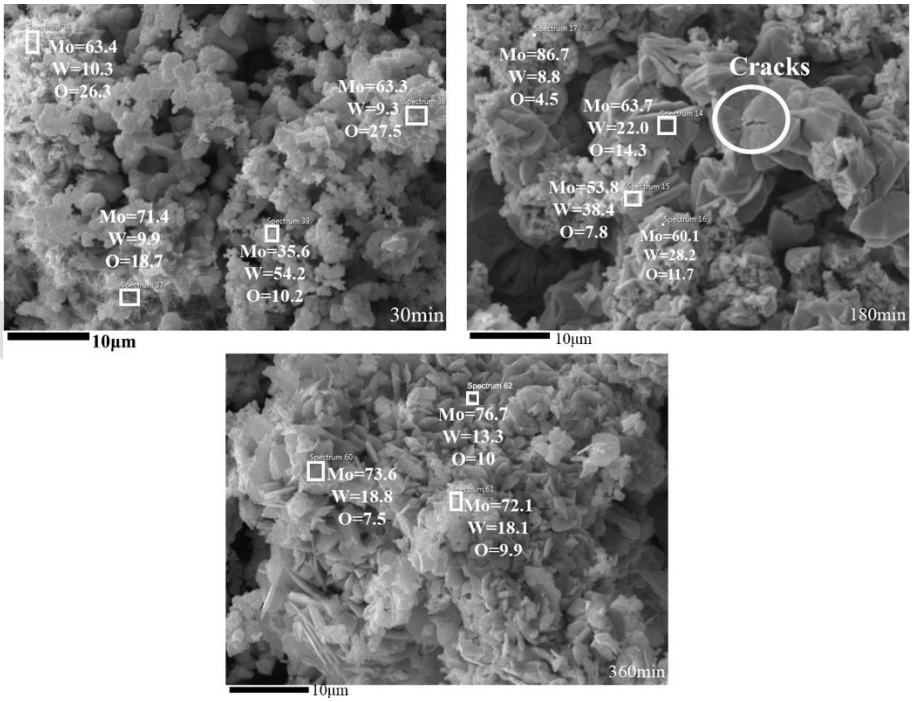

Fig 11- EDAX analysis of the reduced sample MoO_3-26.5wt% WO_3 at 700°C

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Comparing images 10 and 11 with Fig. 15 (oxides mixture EDAX analysis) shows noticeable changes in particle shape at both 600°C and 700°C. Increasing the holding time at these temperatures leads to more significant changes. As previously mentioned, EDAX analysis is not ideal for precisely identifying elements, especially oxygen. However, as expected, the oxygen content in the particles decreased as temperature and time increased. In Figure 11, at T=700ºC and 180 min, some particles show cracks. When the duration extends to 360 min, these cracks disappear, leading to significant changes in particle shape. The cracks indicate the CCM mechanism during H_2 reduction, which is seen in particles with higher molybdenum levels. The CCM in the hydrogen reduction of molybdenum oxide has been confirmed [16].

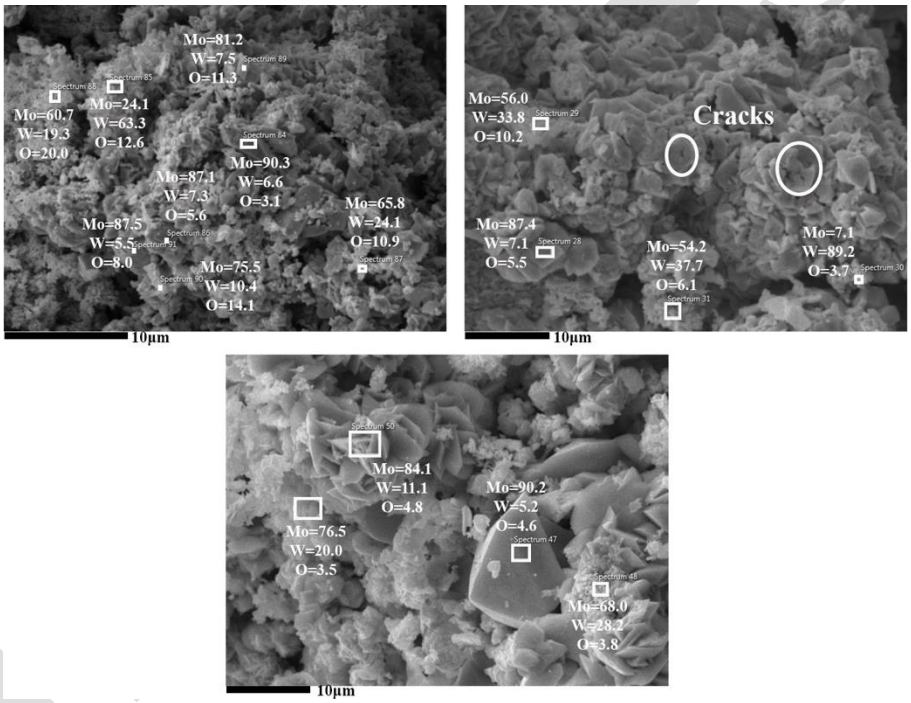

Fig 12- EDAX analysis of the reduced sample MoO_3-26.5wt% WO_3 at 800°C

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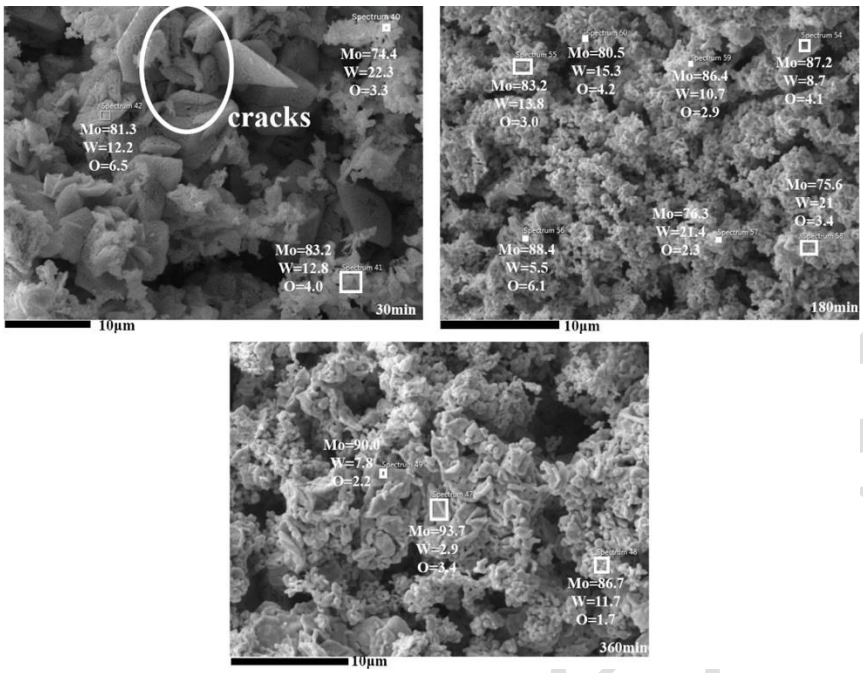

Fig 13- EDAX analysis of the reduced sample MoO_3-26.5wt% WO_3 at 900°C

As shown in Fig.12, at T=800°C and t=180 min, some cracks are visible in the particles, similar to the oxide mixture reduced at 700 °C and 180 min. These cracks are usually caused by the formation of volatile phases from molybdenum or tungsten oxides.

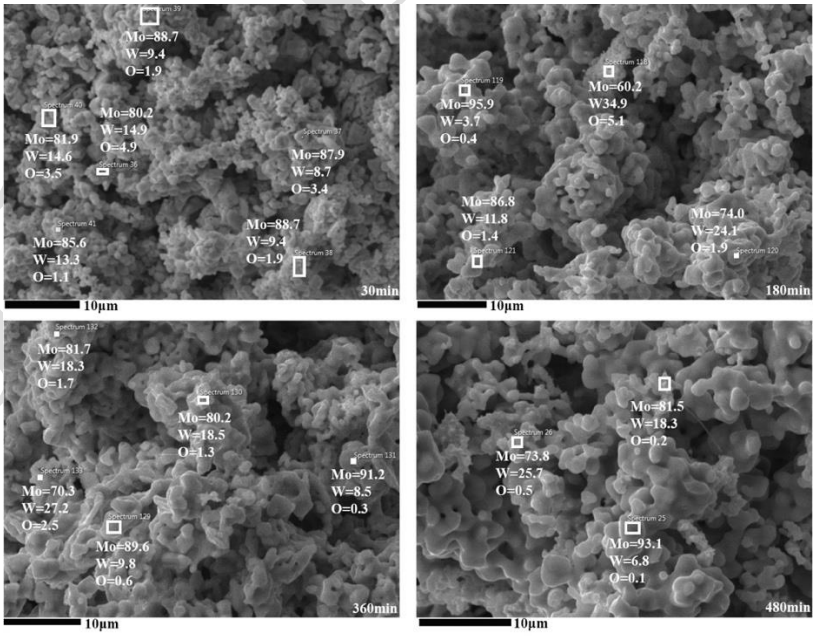

Fig 14- EDAX analysis of the reduced sample MoO_3-26.5wt% WO_3 at 1050°C

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As noted, this mechanism has been reported in the hydrogen reduction of molybdenum oxide; the reduction of tungsten and molybdenum oxides produces intermediate gaseous compounds. Interestingly, at 700°C and 800°C, no cracks appear at 30 minutes of reduction, but they appear at 180 minutes. At 900°C, cracks form after just 30 minutes. By 1050°C, the particles' shape changes significantly, and cracks become much less noticeable.

At 900°C, after 180 minutes, the morphology has not changed significantly, and by 360 minutes the oxygen content decreases. At 1050°C, with increasing time to 480 minutes, the oxygen content decreases. Also, at this temperature, after 180 minutes the morphology and oxygen content do not differ markedly. However, even at 1050°C and 480 minutes, different areas of the sample still do not exhibit uniform chemical composition. Thus, increasing time to 480 minutes did not lead to the formation of alloy particles with a homogeneous chemical composition. Overall, across all samples, the elements molybdenum and tungsten are present at varying levels. Another noteworthy observation is that cracks in the particles are no longer seen at T=1050°C for 30 minutes, indicating that most of the molybdenum and tungsten dioxide phases are no longer in the system. It should also be noted that although the phase transformation of WO_3 and MoO_3 into MoO_2 and WO_2 is nearly complete at 700°C and 800°C within 30 minutes, the formation of cracks in the particles takes longer. Therefore, it can be concluded that the presence of MoO_2 and WO_2 phases is essential for crack formation in the CCM mechanism. These cracks do not form during the reduction of trioxide phases. Instead, vaporization of molybdenum dioxide and tungsten dioxide leads to cracking due to the separation of Mo or W oxides from the particles. The reduction of MoO_3 (or WO_3) by H_2 lowers the oxygen content in the crystal structure, and once the oxygen level reaches a critical point, a new phase with a different crystal structure forms. As shown in the phase analysis, at 600°C after 60 minutes and at 700°C after 30 minutes, the phases MoO_3 and WO_3 are transformed into MoO_2 and WO_2. MoO_2 and WO_2 are crucial for forming intermediate gaseous compounds from molybdenum and tungsten oxides. It should also be noted that after cracks form, the reduction of molybdenum oxide and tungsten oxide continues through the CVT (Chemical Vapor Transport) mechanism. The CVT mechanism has been reported during the reduction of molybdenum and tungsten oxides by hydrogen [23]. The formation of oxide vapor compounds causes mass transfer between points in the reduction system, which can lead to alloy formation. However, the feasibility of producing the alloy by decomposition or reducing the mixture of tungsten and molybdenum vapor compounds by other methods has been confirmed. Also,

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nanostructured W–Mo alloy powders of variable compositions (20-40%Mo) were synthesized by a simple and single-step thermal decomposition process. But Mixture was prepared by $W(CO)_6$ and $Mo(CO)_6$ in different proportions along with diphenyl ether (as solvent. As a result, $W(CO)_6$ and $Mo(CO)_6$ decomposed to form W and Mo, which react together to produce W–Mo alloys [7].

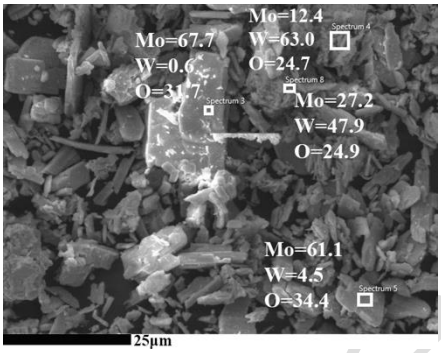

Fig 15- EDAX analysis of MoO_3-26.5wt% mixture

In general, although molybdenum and tungsten were detected together throughout the reduced samples, chemical homogenization through isothermal oxide reduction was ineffective, even at 1050 °C for 480 min. The formation and reduction of volatile molybdenum and tungsten hydroxy species should therefore be considered a key factor improving chemical homogeneity. Because molybdenum and tungsten have high similarity in the chemical properties and crystal structures, it is reasonable to assume that volatile molybdenum species can be reduced on tungsten-containing particles and volatile tungsten species can be reduced on molybdenum-containing particles. So, the formation of a vapor phase from molybdenum and tungsten oxides during hydrogen reduction, followed by their subsequent reduction and deposition onto each other, improves chemical homogeneity. Therefore, to enhance the chemical homogeneity of pre-alloyed powder, the reduction conditions should be adjusted to allow tungsten and molybdenum vapor hydroxy compounds to reduce for a longer time. This longer time will allow these compounds to be transported to particles farther from their site of formation. Based on the experimental data, the lowest temperature and holding time at which only metallic phases remained, with no detectable oxide phases, were 800 °C and 180 min. However, at 600 °C for 360 min, MoO_2 and WO_2 were still present, and at 700 °C for 360 min, MoO_2 was still detected. Figures 11 and 12 showed cracks and morphological changes associated with volatile-species formation at 700 and 800 °C for holding times up to 180 min. Therefore, in the 700–800 °C range, metallic phase formation

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proceeds at a lower rate, unlike the rapid reduction observed at 900 and 1050°C (Figures 7&8). Because oxide reduction above 600 °C occurs via the CVT mechanism, a reduction schedule that maintains dioxide phases for a sufficient time should enhance mass transport and improve chemical homogeneity. The temperature range must therefore be selected to allow both the formation of gaseous oxide species and their relatively gradual reduction. Based on these considerations, a modified reduction process was designed for the MoO_3–26.5 wt.% WO_3 mixture.

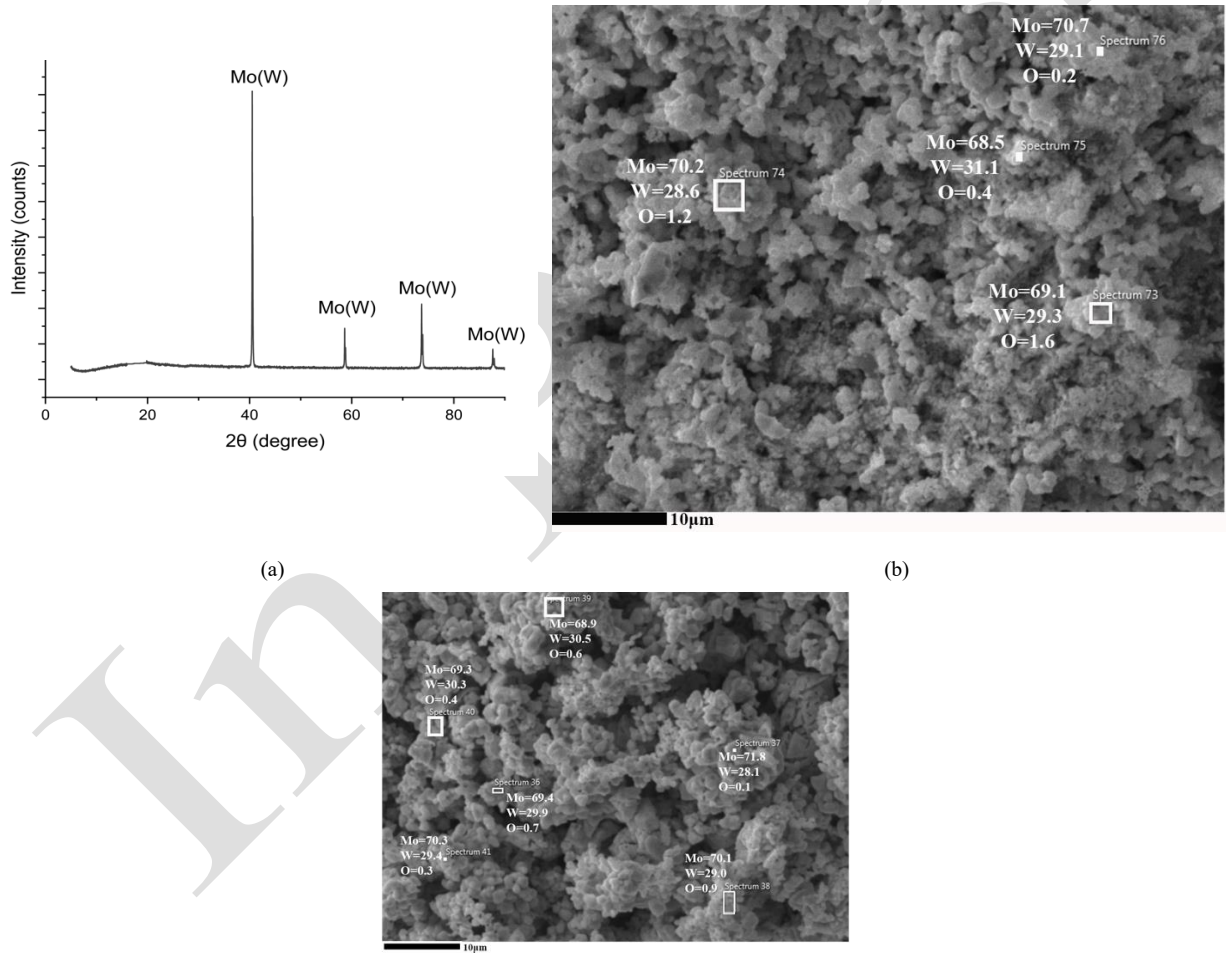

Fig 16- X- ray pattern (b) EDAX analysis of reduced MoO_3-26.5%WO_3 mixture by 600°C,60min+600°C to 1050°C during 240minutes+1050°C,180 min (optimum condition) (c) EDS analysis of the duplicate oxide sample reduced under optimal conditions

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First, the sample was heated to 600°C for 60 minutes to facilitate the formation of MoO_2 and WO_2. These oxides are necessary for the formation of volatile species during hydrogen reduction. The temperature was then gradually increased from 600 to 1050 °C for 240 min. A heating duration of 240 minutes is suitable for the formation of volatile hydroxy compounds and for slow reduction. Finally, to complete the reduction and decrease the dissolved oxygen content, the temperature was held at 1050 °C for 180 min. The resulting weight loss was approximately 30.8%. The XRD pattern and EDAX analysis of the reduced product are shown in Fig. 16.

As shown in Figure 16(a), the XRD pattern of the reduced product shows a single-phase peak, indicating the Mo phase. Although the peaks of molybdenum and tungsten are close to each other, due to the Vol.% of molybdenum, the peak should belong to molybdenum. Furthermore, the EDAX analysis of the reduced product indicates greater homogeneity across different points of the product compared to other reduction cycles. This clearly supports the validity of the proposed hypothesis for improving the homogeneity of the alloy. To verify the optimal conditions and evaluate reproducibility, an additional sample was reduced under the same optimal conditions. The EDS analysis result for this sample is presented in Fig. 16 (c). In this case as well, the XRD pattern was observed to be single-phase, similar to that shown in Fig. 16(a). As shown in Fig. 16 (c), this sample also exhibited satisfactory homogeneity, and its data were in good agreement with those of the first sample (Fig. 16 (b)). For a better assessment of chemical homogeneity, elemental mapping analysis was conducted on the first sample, reduced under the optimal conditions. The corresponding results are presented in Fig. 17. As observed in the elemental maps, both tungsten and molybdenum are distributed throughout all regions of the sample, with nearly uniform elemental intensities across the entire analyzed area. Furthermore, EDS analyses obtained from multiple points revealed compositions close to the nominal Mo–30 wt.% W alloy, confirming the chemical homogeneity of the sample. These results indicate that the applied reduction cycle successfully produced the desired Mo–30 wt.% W alloy powder with a homogeneous chemical composition.

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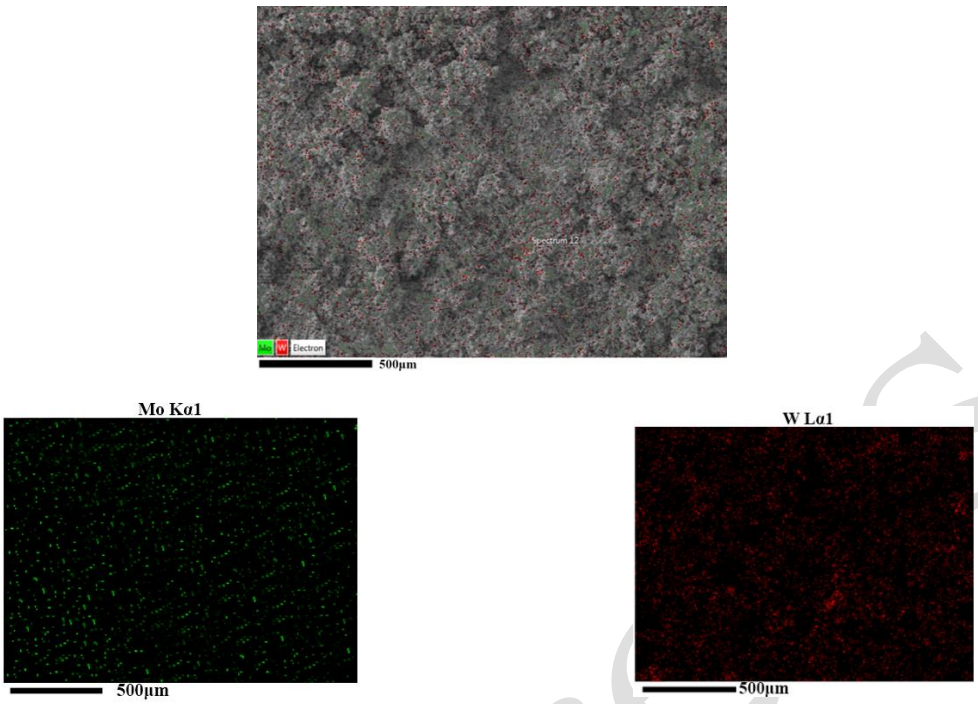

Figure 17- elemental map of MoO_3-26.5 wt.%WO_3 after reduction (600°C,60min+600°C to 1050°C during 240minutes +1050°C,180min)

Therefore, it can be concluded that the applied reduction cycle (600 °C for 60 min, followed by heating from 600 to 1050 °C over 240 min, and then holding at 1050 °C for 180 min) is suitable for the production of Mo–30 wt.% W alloy powder.

SUMMARY

Based on the hydrogen reduction of MoO_3–26.5 wt.% WO_3 mixtures (for obtaining Mo-30 wt.% W), the following conclusions can be drawn. Holding at 600 °C for 60 min was sufficient to prevent the evaporation or melting of molybdenum oxide by promoting the conversion of MoO_3 to MoO_2. A reduction schedule consisting of a 600 °C step followed by a 1050 °C hold for 180 min was effective for the complete reduction of the mixed oxides, similar to the behavior observed during separate oxide reduction. For this reduction cycle, EDAX analysis proves decreasing of oxygen content of the mixture after 180 minutes. By reducing at 800°C<T<1050°C and 180min<t<360min, it can be said that metallic tungsten and molybdenum are present in all particles. However, a fully homogeneous distribution of tungsten and molybdenum was not achieved under isothermal conditions. During the hydrogen reduction of mixed tungsten trioxide and molybdenum trioxide, volatile molybdenum and tungsten oxide species were formed. These

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volatile species, such as $MoO_2(OH)_2$ and $WO_2(OH)_2$, are typically produced from molybdenum dioxide or tungsten dioxide in the presence of water vapor and are subsequently reduced by hydrogen. The results suggest that Mo–W alloying occurs through the reduction of volatile oxide species after each element deposits on the other element after reduction of volatile oxide species. So, these species facilitate mass transfer between tungsten and molybdenum during reduction. Cracks due the formation of vapor species were clearly observed during the reduction of the oxide mixture at T=700&800°C. Therefore, it can be concluded that the formation of these cracks results from the generation of volatile molybdenum and tungsten oxide compounds from their respective dioxide compounds. It is especially important to adjust the reduction conditions to allow sufficient time for Mo and W distribution via the CVT mechanism. Because $MoO_2(OH)_2$ and $WO_2(OH)_2$ form from $MoO_2/WO_2 + H_2O$, and reduction occurs rapidly above 800°C, whereas dioxide phases form at 600°C, gradual heating from 600 to 1050 °C was found to be suitable for improving chemical homogeneity. The optimum cycle consisted of holding the MoO_3–26.5 wt.% WO_3 mixture at 600 °C for 60 min, gradually increasing the temperature to 1050°C over 240 min, and finally holding at 1050°C for 180min to complete reduction. This schedule provided sufficient time for volatile molybdenum and tungsten compounds to contribute to mass transport, resulting in a more homogeneous distribution of the alloying elements across the powder particles.

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