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Effect of ethanol on the formation and properties of a Cu–NbC composite

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ABSTRACT

Copper (Cu), niobium (Nb) and graphite (C) powders were used as starting materials to produce an in-situ Cu–15 vol% NbC composite using mechanical alloying followed by spark plasma sintering (SPS). A mixture of Cu, Nb and C powders was milled in an argon atmosphere for 30 h. Different amounts of ethanol were used to study the effect of the process control agent on the formation of NbC and the consequent properties of the Cu–NbC composite. The results showed that NbC was formed in the copper matrix during ball milling when the powders were milled with 0–2 wt% ethanol, whilst the powder milled with 5 wt% ethanol only exhibited NbC formation after sintering. The as-milled powders were then sintered using SPS at 1000 °C, an applied pressure of 100 MPa and soaking duration of 15 min. As a result, the best combination of properties was observed in the sintered Cu–15 vol% NbC composite using a powder milled with 1 wt% ethanol, viz. electrical conductivity of 24% IACS, microhardness of 377 Hv and relative density of 97%.

1. Introduction

Mechanical alloying (MA) is a solid-state powder processing method which involves repeated cold welding and fracturing of particles as a result of high energy ball-powder collisions. MA is a suitable technique for the development of metal matrix composite (MMC) materials with superior properties [1,2]. By using this process, very fine reinforcement particles (of nano-scale) were homogeneously distributed within the metal matrix. This led to enhanced mechanical properties and thermal stability of the composite materials [3–5]. An Al–Al_3Ti nanocomposite was reportedly synthesized by mechanical alloying of Al and Ti powders [6]. This composite showed a very high hardness value of 347 Hv after annealing at 400 °C. Another research work [7] showed that the hardness of an Al–1 vol.% nanoSiC composite could be increased from 47 Hv for pure aluminium to 163 Hv when milled at the highest input energy levels.

In mechanical alloying, process control agents (PCAs) play a significant role in controlling the particle size and degree of cold welding during ball milling. A process control agent is a surface additive used in the milling process in order to control the balance between the fracturing and cold welding of particles. The alloying process can only be continued if the rate of welding and fracturing are balanced and the average particle size of the powders remains relatively coarse. Lu and Zhang [8] reported that the reaction between Al and Mg in his system decreased with an increase in the amount of PCA. When the amount of PCA was above 3%, the degree of reaction dramatically decreased. In addition, PCA did not only affect the alloying process but also affect the formation of solid solution during mechanical alloying. A research work reported for a Cu–Cr powder system showed that the formation of a Cu(Cr) solid solution was more pronounced when milling was carried out in the presence of a PCA [9]. There are several PCAs which were often used in MA such as heptanes, ethyl acetate, ethylenebidi-steramide, polyethylene glycol, methyl alcohol and ethyl alcohol [10,11]. Currently, the increasing attraction on Cu–NbC composites is due to its high electrical conductivity and high strength [12–14]. However, the authors could not find any research work on the effect of PCAs on the formation of NbC and the consequent properties of Cu–NbC composites that are synthesized by the mechanical alloying process.

Spark plasma sintering (SPS) is a potential consolidation technique to be used for sintering as-milled Cu–NbC powders. SPS is a field-activated sintering technique. The SPS process is similar to a conventional hot pressing. However, instead of external heating, a pulsed direct current is passed through a graphite die that holds the powder whilst mechanical uniaxial pressure is applied simultaneously during sintering. In this technique, the graphite die becomes a heat source, and the sample is heated from both the outside and inside of the die. Details on the SPS process was reported elsewhere [15]. SPS can also be used with high heating and cooling rates, and in shorter processing duration [16,17] which resulted in the achievement of full theoretical density with minimal grain-growth [18].

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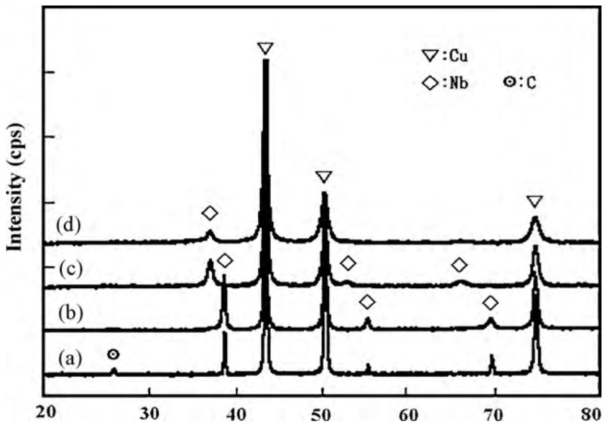

Fig. 1. XRD patterns of Cu–15 vol% NbC mixture with 5 wt% ethanol for different milling duration of: (a) 0 h, (b) 1 h, (c) 5 h and (d) 30 h.

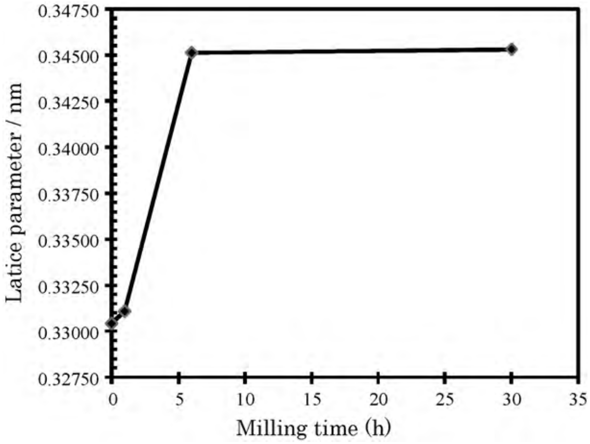

Fig. 2. The change in lattice parameter of Nb with different milling duration of 0, 1, 5 and 30 h.

In this research work, a mixture of Cu, Nb and C powders with a composition corresponding to 15 vol% NbC was subjected to ball milling. Ethanol was used as the process control agent in varying amounts of 0, 1, 2 and 5 wt% to evaluate the effect of ethanol on the formation of NbC and the consequent properties of the Cu–NbC composite.

2. Experimental procedures

The staring materials used in this research work were Cu, Nb and C powders with a composition corresponding to Cu–15 vol% NbC. Cu powder was of 99.9% purity with an average of particle size ≤180 μm, Nb powder was of 99.5% purity and with particle size ≤7 μm, whilst C powder was of 99.9% purity and with particle size ≤10 μm. Ethanol was used as the process control agent in varying amounts of 0, 1, 2, and 5 wt% in order to prevent excessive cold welding of these powders during ball milling.

The loading and discharging of the powders from the milling containers were carried out in a glove box with Ar atmosphere to prevent oxidation of the powders. The powders were milled in two steel containers of 500 ml using a Fritsch "Pulveristte 5" planetary ball mill at a rotation speed of 250 rpm. The mixture of Cu, Nb and C powders was milled under Ar atmosphere for 1, 5 and 30 h. The balls used were 10 mm in diameter and the powder-to-ball weight ratio was 1:10. In order to study the effect of ethanol on the formation of NbC and the properties of Cu–NbC composites consolidated by SPS, the as-milled powders were sintered using a Dr. Sintering@ 2040 spark plasma sintering system (Sumitomo Coal Mining, Tokyo, Japan) at 1000 °C, 100 MPa for 15 min in a vacuum atmosphere of 5 Pa.

The as-milled powders and sintered compacts were characterized by energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) for chemical and phase identifications. Lattice parameters of Nb and Cu were calculated from the XRD patterns using the (1 1 0) and (1 1 1) peaks for Nb and Cu, respectively. The microstructures of the composites were investigated using optical microscopy (OM) and scanning electron microscopy (SEM). The hardness and electrical conductivity were measured using a Vicker's microhardness tester and an Ulvac ZEM 1 electrical conductivity equipment, respectively. Electrical conductivity is measured using the IACS unit whereby IACS refers to the International Annealed Copper Standard and 100% IACS is equal to 58.0 m/Ω mm^2. The density of the sintered samples was measured using the Archimedes' method.

3. Results and discussion

3.1. The formation Nb(C) solid solution during ball milling

The XRD pattern of the starting materials is shown in Fig. 1(a) which clearly shows the peaks of Cu, Nb and C. The XRD patterns of Cu, Nb and C powder mixtures milled for different milling duration of 1, 5 and 30 h with 5 wt% ethanol are also shown in Fig. 1(b)–(d).

The positions of the XRD peaks of Nb are almost unchanged after milling for 1 h, and these peaks show high intensity due to the existence of low strain and the particle size being coarse, as shown in Fig. 1(b). The XRD peaks of Nb become broadened after further milling for 5 and 30 h due to powder refinement and high strain. It is also noticed that the positions of the Nb peaks are shifted after milling for 5 h. The main Nb peak is shifted from 38.4° to 37.0° 2θ, as shown in Fig. 1(c). In the case of 30 h milling, the position of the main Nb peak does not change as much compared to the 5 h-milled powder, the shift is only from 37.0° to 36.8°, as shown in Fig. 1(d). These results indicate that C formed a solid solution in Nb during ball milling. This suggestion can be proven by plotting the Nb lattice parameter versus milling duration, as shown in Fig. 2. The lattice parameter of Nb is 0.33042 nm before milling. The lattice parameter increases slightly to 0.33109 nm after milling for 1 h but it is significantly increased to 0.34512 nm after milling for 5 h. The lattice parameter of Nb almost does not change when milling was carried out for 30 h. This can considered as an indication that almost all of the solid solution formation takes place after 5 h of milling.

In this work, NbC was not formed during ball milling when 5 wt% ethanol was used as the process control agent. However, the equilibrium thermodynamic data of Gibbs free energy for NbC formation, ΔG_f is equal to $-137\ \mathrm{kJ\,mol^{-1}}$ at 300 K which indicates the feasibility of the reaction between Nb and C taking place at room temperature. Therefore, it can be concluded that the reason for the non-formation of NbC is due to the formation of a solid solution of C in Nb as supported by a previous work [19].

3.2. Effect of ethanol on the formation behavior of NbC

In order to understand the effect of ethanol on the formation of NbC during ball milling, different Cu, Nb, and C powder mixtures were milled with different amounts of ethanol (0, 1, 2, and 5 wt%) for 30 h. The morphologies of the as-milled Cu–Nb–C powders are shown in Fig. 3. It can be easily observed that finer as-milled Cu–Nb–C powder particles are achieved when the mixtures were milled with increasing amount of ethanol. The finest of the as-milled Cu–Nb–C powder particles is obtained in the sample which was milled with 5 wt% ethanol as the process control agent, as shown in Fig. 3(a). The size of the as-milled Cu–Nb–C powder particles increases with decreasing amount of ethanol, as shown in Fig. 3(b)–(d). During ball milling, the powder had undergone cold welding and fracturing processes due to the collision between ball-powder-ball and ball-powder-wall. However, the fracturing process seems dominant in the sample using 5 wt% ethanol. In this sample, the amount of ethanol is sufficient enough to cover the surfaces of the powder particles, and helps to inhibit excessive cold welding. It was reported that the lower surface tension of the particles resulted in finer powder particles being produced [20].

When the amount of ethanol is less than 5 wt% during milling, such as 1 and 2 wt%, the cold welding process becomes more domi-

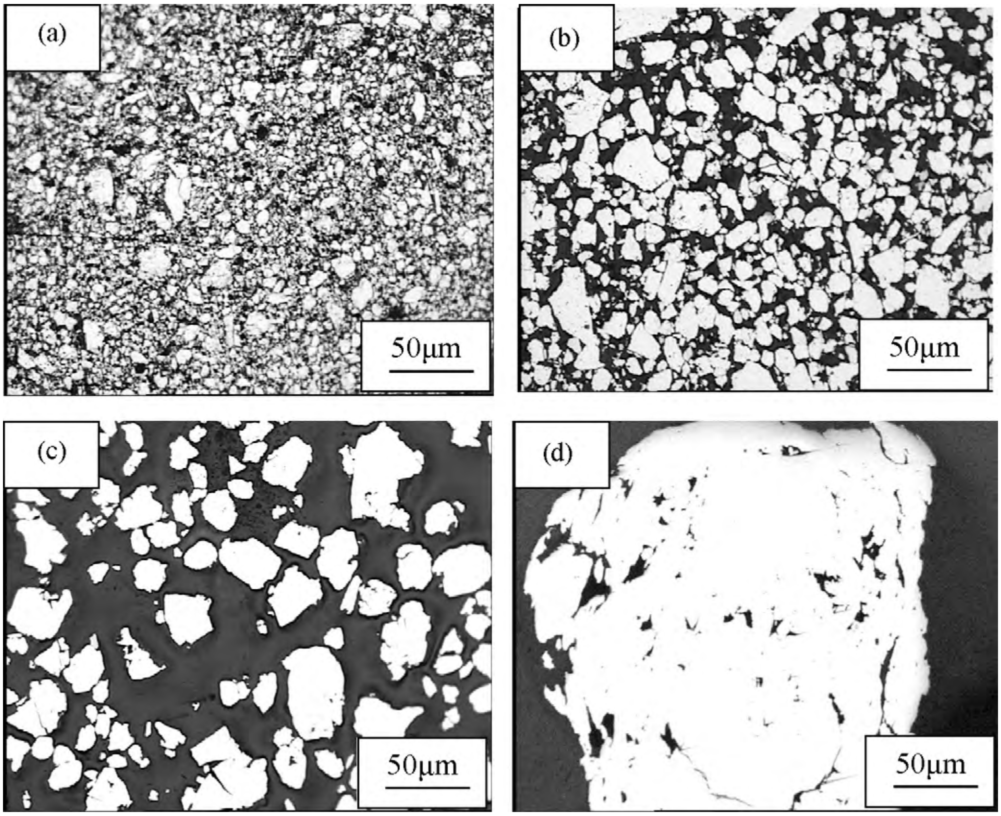

Fig. 3. Optical micrographs of as-milled Cu–Nb–C powder with different amounts of ethanol (a) 5 wt%, (b) 2 wt%, (c) 1 wt% and (d) 0 wt% after milling for 30 h.

nant than the fracturing process. It is likely to cold weld the powder particles together rather than fracturing. Subsequently, the cold welding process becomes almost dominant in the sample which was milled without ethanol. It means that the particles had undergone plastic deformation and cold welding. The excessive cold welding process brought the particles together into a aggregated form.

The XRD patterns of Cu, Nb and C powder mixtures with different amounts of ethanol are shown in Fig. 4. The main XRD peak of Nb which is at 38.4° 2θ shifts to a lower Bragg's angle of 36.8° 2θ when milling was carried out with 5 wt% ethanol, as shown in Fig. 4(b). There are no NbC peaks detected in this sample. As mentioned earlier, this is attributed to the fact that Nb and C completely formed Nb(C) solid solution. NbC phase starts to form when ethanol was reduced to 2 wt%, as shown in Fig. 4 (c). The XRD peaks of NbC become more distinct whilst the XRD peaks of Nb become lower in intensity when the powder mixture was milled with 1 wt% ethanol, as shown in Fig. 4(d). Nb still exists and the position of the Nb peak is also shifted from 38.4° to 36.8° in both powders indicating that the formation of both NbC and Nb(C) took place during ball milling. The XRD peak of Nb completely disappears when milling was performed without ethanol addition, indicating that the only reaction between Nb and C was to form NbC in this powder. There is no formation of Nb(C) solid solution, as shown in Fig. 4(e).

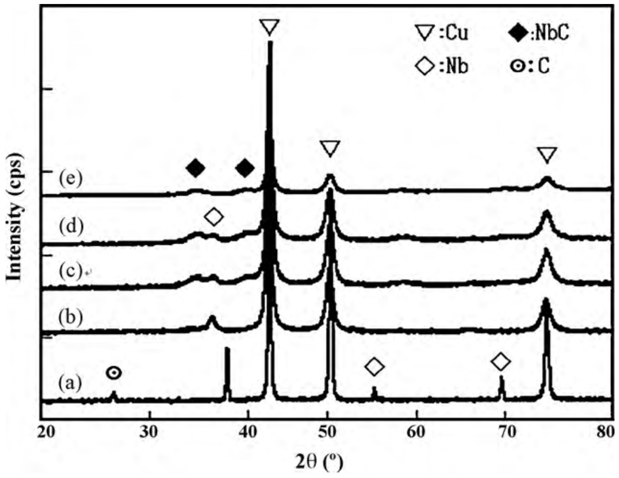

Fig. 4. XRD patterns of (a) Cu–Nb–C powder mixture without ethanol, and as-milled powders with different amounts of ethanol (b) 5 wt%, (c) 2 wt%, (d) 1 wt% and (e) 0 wt% after milling for 30 h.

The effect of ethanol on the formation of NbC during ball milling can explain the mechanisms that took place during the mechanical alloying process. In MA, essentially two competing processes are involved which are, cold welding between particle and particle, as well as fracturing of cold welded particles under high impact energy [8]. In this research work, the use of a high amount of ethanol, i.e. 5 wt%, has led to the domination of the fracturing process of the powder particles during ball milling which resulted in finer particles, specifically Nb. The diffusion process of C into Nb is negligible because the particles are always fragmenting. Therefore, the collisions between the balls and particles have generated high impact energy to diffuse C into Nb to form a solid solution. In the case of milling the Cu–Nb–C mixture without ethanol, the cold welding and plastic deformation processes predominated at the earlier stages of ball milling which led to Nb and C particles being welded together to a minimum distance. Hence, under this condition, diffusion could take place easily [8]. In addition, the reaction between Nb and C was also prompted by the high impact energy during ball milling [21]. This impact energy from collision between ball and powder activated the reaction and led the reaction to take place faster without necessitating the need for sintering.

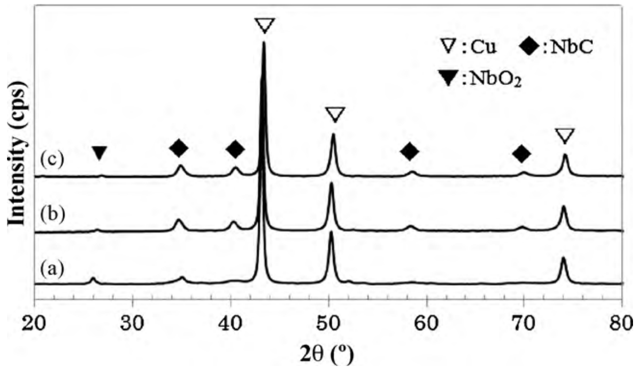

Fig. 5. XRD patterns of sintered Cu–15 vol% NbC with different percentages of ethanol, SPS at 1000 °C, 100 MPa, and 15 min: (a) 5 wt%, (b) 2 wt% and (c) 1 wt% ethanol.

Table 1
EDX data of Cu–NbC composite using different percentages of ethanol.

Cu-15 vol% composite, 1 wt% ethanol, SPS, 1000 °C, 100 MPa, 15 min, 100 °C/min	
Elements	wt%
C	8.35
O	0.694
Nb	13.354
Fe	1.014
Cu	76.578
Cu-15 vol% composite, 5 wt% ethanol, SPS, 1000 °C, 100 MPa, 15 min, 100 °C/min	
Elements	wt%
C	4.786
O	1.266
Nb	10.756
Fe	0.558
Cu	82.632

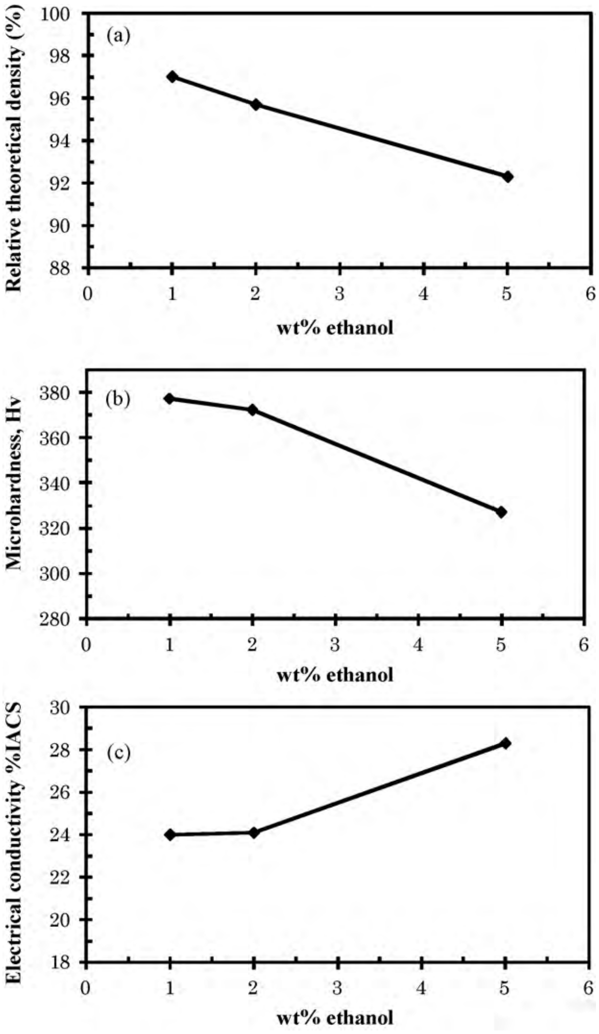

Fig. 6. Properties of Cu–15 vol% NbC composite using different amounts of ethanol, SPS at 1000 °C, 100 MPa, 15 min, 100 °C/min.

Table 2
Comparison of properties with another research work [4].

Composite	Electrical conductivity (%IACS)	Microhardness (Hv)	Theoretical density (g/cm^3)
Cu–15 vol% NbC	24.0	377.1	97.0%
Cu–77 vol% TiC	2.24	544.0	93.4%

3.3. *Effect of ethanol on the properties of Cu–NbC composite*

Fig. 5 shows the XRD patterns of Cu-NbC composites sintered using SPS on as-milled powders with different amounts of ethanol. It can be seen that NbO_2 is observed for composites containing 2 wt% and 5 wt% ethanol. The intensity of the NbO_2 peak decreases when decreasing amount of ethanol was used and NbO_2 peak is no longer observed at 1 wt% ethanol. The intensity of NbC peaks are significantly increased when less amount of ethanol was used. These results suggest that the oxygen is sourced from ethanol, C_2H_5OH. Ethanol was decomposed into C_2H_4 and H_2O during sintering [22]. This conclusion is in agreement with other researchers [23] who used process control agents during ball milling.

The relative density of the sintered composite is shown in Fig. 6(a). It is observed that the density of the Cu–15 vol% NbC composite achieve 97.0% of the theoretical density when 1 wt% ethanol was used as the process control agent. The result of Vicker's microhardness is shown in Fig. 6(b). A high microhardness value of 377 Hv is also obtained with the addition of 1 wt% ethanol. However, the electrical conductivity of Cu–NbC composite decreases with decreasing amount of ethanol (Fig. 6c). This is due to the fact that a higher amount of copper was observed to be welded onto the wall of the container when less ethanol was used during milling. The lost weight of copper in the composite was analyzed by EDX, as shown in Table 1. Excessive cold welding of copper onto the container had led to the loss of copper which results in a decrease of copper content which consequently reduces the electrical conductivity of the composite. The microhardness and density of the Cu–NbC composites decrease since the higher amount of ethanol used during ball milling results in high porosity and oxidation. Based on these results, the appropriate amount of ethanol to be used as the process control agent should be 1 wt%. The electrical conductivity in this research work is about 10 times higher compared to a work on Cu–TiC composite [4]. The density in the present work is also higher by comparison. However, the lower microhardness value in present work can be attributed to the fact that 15 vol% NbC reinforcement was used as compared to 77 vol% TiC in that work, as shown in Table 2.

4. Conclusions

Nb and C only formed Nb(C) solid solution in the copper matrix after ball milling Cu–Nb–C powder mixture with 5 wt% of ethanol, whilst both Nb(C) solid solution and NbC were formed when 2 and 1 wt% ethanol were used. After ball milling without ethanol, only NbC was formed in-situ in the copper matrix. The particle size of as-milled Cu–Nb–C powder increases with decreasing amount of ethanol. The powder particles coalesced when milled without ethanol. The optimum amount of ethanol to be used as the process control agent to prevent cold welding during ball milling is 1 wt%.

Electrical conductivity decreases when less ethanol was used due to the higher loss of copper onto the wall of the container. The density and Vicker's microhardness decrease when higher amount of ethanol was used due to higher porosity and oxidation. A high density of 97.0% relative to the theoretical density was achieved in the composite which used 1 wt% ethanol. A high microhardness value of 377 Hv and 24% IACS in electrical conductivity were also obtained in this composite.

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