Research Article

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The formation kinetics of \( \text{Cr}_2\text{O}_3 \) dispersed \( \text{Cu} \) synthesized by Cryo-milling

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Abstract: Nano-crystalline (nc) \( \text{Cu} \) with \( \text{Cr}_2\text{O}_3 \) dispersoid (~4 vol.%) was successfully made by reactive-milling at 210 K with a mixture of pure \( \text{Cu} \), \( \text{Cu}_2\text{O} \), and \( \text{Cr} \) powder. The vacuum hot pressing (HP) was performed at 1123 K and 50 MPa for 2h to consolidate the milled powder for further analysis. TEM (Transmission Electron Microscopy) work revealed that the HPed materials were comprised with a mixture of the nc-\( \text{Cu} \) and a homogeneous distribution of \( \text{Cr}_2\text{O}_3 \) dispersoids. The microstructure and Vickers hardness of the as-milled powder and the HPed materials were characterized by standard metallographic techniques. The \( \text{Cr}_2\text{O}_3 \) dispersoid size was estimated from the HADDF (High Angle Annular Dark Field) images and element mapping by STEM-EDS (Scanning Transmission Electron Microscopy-Energy Dispersive Spectroscopy) works. The formation kinetics and coarsening of the \( \text{Cr}_2\text{O}_3 \) dispersoids in \( \text{Cu} \) matrix were discussed based on the calculations with thermodynamic parameters in comparison with those of \( \text{Al}_2\text{O}_3 \).

Keywords: Cryo-milling; Oxide Dispersed Copper; Formation of \( \text{Cr}_2\text{O}_3 \)

1 Introduction

Oxide dispersion strengthened (ODS) \( \text{Cu} \)-based alloys have been paid much attentions for their good thermal, electrical, and mechanical properties in the fields of nuclear, electronic, and spot welding in auto industry [1, 2]. The strength of ODS materials are originated from the fine oxide to give rise to the interaction with dislocations and grain boundaries. Among the oxide dispersoids, nano-sized \( \text{Al}_2\text{O}_3 \) or \( \text{Y}_2\text{O}_3 \) particles has been frequently selected to avoid the dispersoid coarsening at the processing and operating temperatures [3]. These fine dispersoids would be an effective obstacle not only to the dislocation movements but also to grain coarsening. As suggested by Groza in early 1990’s [2], the prime candidates for the most stable oxide dispersoids are considered by their large negative heats of the formation and the high melting points. There are many reports on the ODS \( \text{Cu} \) with \( \text{Al}_2\text{O}_3 \) and \( \text{Y}_2\text{O}_3 \) dispersoids, whereas a limited number of published papers are found on ODS \( \text{Cu} \) with \( \text{Cr}_2\text{O}_3 \) [4, 5].

The \( \text{Y}_2\text{O}_3 \) dispersoids has an attraction for the highest enthalpy of formation to keep themselves to be fine and small; \( \text{Al}_2\text{O}_3 \) dispersoids has a forte for the versatile processing (the internal oxidation and/or Mechanical Alloying). However, it seems that insufficient examination has been made to take advantage of using \( \text{Cr}_2\text{O}_3 \) instead of \( \text{Al}_2\text{O}_3 \) or \( \text{Y}_2\text{O}_3 \). We have paid attention on the Shojaeepour’s propose [5] that the internal oxidation or MA process for the ODS \( \text{Cu} \) might be complex; it ended up with being incomplete process. This may lead to dissolution of remnant \( \text{Al} \) into the \( \text{Cu} \) during high temperature processing; the degradation of the electrical conductivity possibly happens for the high solute contents of \( \text{Al} \) in \( \text{Cu} \). On the contrary, \( \text{Cr} \) in \( \text{Cu} \) with a very limited solubility will not cause this problem; unreacted \( \text{Cr} \) in \( \text{Cu} \) matrix, if any, can be precipitated by a proper homogenizing & annealing to enhance the mechanical properties of the ODS \( \text{Cu} \) alloys.

In this study, we have aimed to produce a \( \text{Cu}-4 \text{ vol.\% Cr}_2\text{O}_3 \)(or \( \text{Cu}-4\text{Cr}_2\text{O}_3 \)) powder by reactive milling, to consolidate them by vacuum HP (hot pressing), and to characterize the microstructure of the materials. We have also compared the \( \text{Cu}-4\text{Cr}_2\text{O}_3 \) with \( \text{Cu}-4 \text{ vol.\% Al}_2\text{O}_3 \) (or \( \text{Cu}-4\text{Al}_2\text{O}_3 \)) materials in terms of the microstructure and hardness before and after hot pressing. The \( \text{Cu}-4\text{Al}_2\text{O}_3 \) materials had been consistently prepared under a same process condition; the comparable results of the microstructure and hardness on the \( \text{Cu}-4\text{Al}_2\text{O}_3 \) were reported on the previous papers [7, 9]. The formation kinetics of the dispersoids is analyzed in terms of thermodynamic consideration; the coarsening behavior of the dispersoids at the processing temperature (HP) is also discussed along with the results of TEM observations.

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Table 1: The released heat of reaction (−ΔH) and the calculated adiabatic temperature (T_{ad}) and incubation time (t_{ig}) to ignite of corresponding displacement reactions.

| Reaction, (number) | Heat of reaction (−ΔH, kJ/mol) | Adiabatic Temp. (T_{ad}, K) | Incubation time (t_{ig}, sec) |
|--------------------|---------------------------------|----------------------------|-------------------------------|
| 3Cu_2O+2Cr → 6Cu+Cr_2O_3, (1) | 633.9 | 2300 | 21,400 |
| 3Cu_2O+2Al → 6Cu+Al_2O_3, (2) | 1169.9 | 3569 | 2,400 |
| 3Cu_2O+2Cr+92Cu → 98Cu+Cr_2O_3, (3) | 633.9 | 539 | >21,400 |
| 3Cu_2O+2Al+77.3Cu → 83.3Cu+Al_2O_3, (4) | 1169.9 | 807 | >2,400 |

Table 2: Vickers hardness, grain sizes of Cu, vol.% of dispersoids, and dispersoid size for the Cu-4Cr_2O_3/4Al_2O_3 [7].

| Materials | Vickers hardness (powder/HPed, VHN) | Grain size of Cu (powder/HPed, nm) | Volume fraction of dispersoid (%), calculated | Dispersoid size (radius, nm) |
|-----------|-----------------------------------|----------------------------------|---------------------------------------------|---------------------------|
| Cu-4Cr_2O_3 | 270±9/135±5 | 14.3±2/30.3±2.5 | 4 | 11.6±3.1 |
| Cu-4Al_2O_3 [7] | 253±7/265±8 | 15.4±1.5/25.1±2 | 4 | 4±0.3 |

2 Experimental

In this experiment, we have used a mixture (100g) of pure Cu (Sigma-Aldrich, -200mesh, 99.5%), Cu_2O (Sigma-Aldrich, -325mesh, 97%), and Cr (Sigma-Aldrich, -200mesh, 99.9%) powder. A weighed mixture of the powder in a molar proportion according to the reaction (3) was loaded in a high energy attritor mill (Table 1). The mill was equipped with water cooling jacket outside and with a high purity Ar atmosphere filled chamber inside. The milling was conducted in Ar (1 bar) with the ball to powder weight ratio (16: 1) at 210 K using liquid nitrogen (LN_2) to cool the mill chamber for the first 2 h. The speed of attritor rotor was controlled to maintain 800 rpm. The LN_2 supply was then switched to tap water for the rest of 14 h to completion of milling.

This reactive milling would derive the formation of Cu matrix with 4 volume % Cr_2O_3 (Cu-4Cr_2O_3) at the completion of the milling, assuming that all of chromium and oxygen has reacted to Cr_2O_3 after the reaction (3) completed. A small portion of milled powder was periodically sampled and monitored by XRD as a function of milling time. The result of XRD patterns of milled powder obtained from milling times up to 16 h is shown in the Figure 1. The contamination of impurities has been always a concern in the milling processes. There were insignificant impurity pick-ups of interest from the XRD and EDS for examination; it is supposed that the level of contamination is very low and undetectable.

A button type of sample (25 mm, Φ × 11 mm) was prepared with the as-milled powder by vacuum hot press (HP) at the 1123 K and 50 MPa for 2 h. The grain size of nc-Cu was calculated from the full width at half maximum (FWHM) of Cu (111) diffraction peak using Scherrer’s formula (presented in the Table 2). The microstructural evolution and phase identification of the materials were monitored by XRD using Cu Kα radiation. TEM specimens were prepared by Focused Ion Beam (FIB) directly from polished surface of the HPed materials. Image analysis of STEM micrographs was performed to characterize the microstructure of the materials. SEM specimens were also prepared for the surface observation of the milled and HPed materials, respectively.

Micro Vickers hardness tests were performed on the milled powder and the HPed materials. The Vickers hardness (H_V) values of the materials exclusive of the highest and the lowest from 10 measurements were reported along with the standard deviation in the Table 2. The previous results [7, 9] of experimental works for the Al_2O_3 dispersed Cu (Cu-4Al_2O_3) including the microstructural and hardness values are presented in comparison with the results of this study (Cu–4 Cr_2O_3) in the Table 2. The details of the processing (milling and consolidation) are found in elsewhere [7, 9].

3 Results and discussions

Figure 1 shows XRD patterns of the milled powder as a function of milling times up to 16 h. The figure illustrates that both Cu_2O and Cr peaks gradually decrease with increasing milling time, which were well below the resolution limit of XRD after 16 h milling. This would be an indicative evidence of the reaction completed. A XRD pattern
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**Figure 1:** XRD patterns of the milled powder obtained as a function of milling times up to 16 h.

**Figure 2:** XRD pattern of the HPed Cu with Cr₂O₃ dispersoids (the peaks of Cu and Cr₂O₃ are clearly identified).

**Figure 3:** TEM micrographs of the as milled powder for 16 h showing the dispersoid produced by reactive milling.

The grain size of the as-milled powder and the HPed materials was estimated by measuring FWHM of Cu (111) diffraction peak using Scherrer’s formula. The result of the measurement is shown in the Table 2 along with the Cu grain size of Cu-4Al₂O₃. It is interesting that the sizes of the Cu grain in both of the Cu-4Cr₂O₃ and the Cu-4Al₂O₃ have not coarsened much even at high temperature (1123 K) processes (HP). It is most likely due to the presence of the Al₂O₃ and Cr₂O₃ dispersoids, which retards Cu grain boundaries not to grow. The presence of Cr₂O₃ peak in the XRD pattern after HP was clearly noticed, which was the suggestive evidence that Cr₂O₃ dispersoids coarsened after HP. In contrast to this result, an insignificant intensity of Al₂O₃ peaks was noticed on the XRD patterns of the Cu-4Al₂O₃ materials [7, 9]. This result agrees with the size distribution under TEM observations on both materials before and after HP. The Table 2 presents the average dispersoid size of Cr₂O₃ and Al₂O₃ after HP; this data evidently shows that the Cr₂O₃ dispersoids are relatively bigger than Al₂O₃. In Figure 3, a TEM micrograph of the as milled powder is present; the Cr₂O₃ dispersoids in the powder interior is extremely fine. No significant difference between the two kinds of powders was observed in the microstructural issue in TEM observations [7]. The TEM results are suggesting that the Cr₂O₃ is coarsening faster than Al₂O₃ while HP.

Figure 4(a) is a typical cross section of the milled powder (Cu-4Cr₂O₃) with the micro Vickers indentation observed by SEM. Figure 4(b) also shows the morphology and size of the milled powder (Cu-4Cr₂O₃). The SEM pictures show that the milled powder are in spherical shape with irregular surface; the cross sections of the powder is thick enough to indent with micro Vickers tester. The Figure 5 is a typical TEM bright field image of the HPed; the corresponding electron diffraction pattern (DP, inset of the Figure 5) obtained from the HPed Cu-4Cr₂O₃ materials. The overall TEM observations reveal that the microstructure of the HPed is free of pores and well homogeneous distribu-
Figure 4: (a) SEM micrograph (left) of cross section of the as-milled Cu-4Cr$_2$O$_3$ powder, showing the indentation of Vickers hardness test (b) A typical SEM picture (right), showing the morphology of the powers.

Figure 5: Bright field image of TEM and corresponding diffraction pattern (Inset of the picture), illustrating the mixture of Cu grains and Cr$_2$O$_3$ oxides.

tion of Cu grains and Cr$_2$O$_3$ dispersoids with a few much coarse one in size on the grain-boundaries. The grain size of the Cu by TEM observation in the HPed material are fairly in agreement with the result of Scherrer’s formula using XRD (Table 2).

By indexing DP taken in the representative area, we have attempted to identify the phases in the materials (Figure 6). The attempts show that diffracted spotty rings are mostly from Cu lattices and the first and second ring from the center are attributed to the presence of Cr$_2$O$_3$. These two diffraction rings are exactly overlapped with the rings from the Cu$_2$O lattice. Both Cu$_2$O and Cr$_2$O$_3$ overlapping on the DP is not a conclusive but only suggestive evidence of Cu$_2$O present. If Cu$_2$O still remains in the Cu matrix unreacted, Cr should be found to meet the balance of the reaction (3). As assumed, a weak diffraction ring from Cr (200) was found; this results suggested that a little Cu$_2$O partially unreacted is also present. The presence of the partially unreacted Cr and Cu$_2$O evidenced by TEM diffraction pattern implies that the milling has not perfectly completed even after 16 h.

A STEM-HAADF image (Figure 7) of the HPed materials illustrates the size and distribution of the dispersoids. The element mapping images of Cu (Figure 7(b)) and Cr (Figure 7(c)) evidences that the dispersoids in the HAADF image are Cr$_2$O$_3$ dispersoids. As presented in the Figure 7(a), most of the coarse dispersoids are found in grain boundaries of Cu, whereas the relatively small dispersoids in grain interior. This explains how the Cr$_2$O$_3$ dispersoids
are preventing the Cu grain from coarsening at the elevated temperatures during HP. No evidence of interactions between the dislocations and fine dispersoids are found in TEM observations. This observation is in disagreement with the case of HP Cu-4Al\(_2\)O\(_3\) materials [7], where a lot of the Orowan loop dislocation was formed as a result of the interaction with a few nano sized Al\(_2\)O\(_3\). The results of micro Vickers test before and after HP are presented in Table 2. The Cu-4Cr\(_2\)O\(_3\) shows a sharp drop of hardness values after HP while the Cu-4Al\(_2\)O\(_3\) does not. As evidenced in TEM observation, the coarsening of Cr\(_2\)O\(_3\) dispersoids is faster; it explains how the hardness drop of the Cu-4Cr\(_2\)O\(_3\) happens while Cu-Al\(_2\)O\(_3\) even increases in hardness after HP.

Now, we are about to discuss the formation kinetics and coarsening behavior of the Cr\(_2\)O\(_3\) and Al\(_2\)O\(_3\) dispersoids in term of thermodynamic consideration. The necessary thermodynamic data from the literatures are given in the Table 1 [11, 12]; the released heat of the reaction (1-4) can be found in Table 1. For an instance, \(\Delta H_{Cu_2O \rightarrow Cr_2O_3}\) for the reaction (1) at 298 K in Table 1 is \(-633.9\) kJ by a calculation as follows:

\[
\begin{align*}
3Cu_2O + 2Cr &\rightarrow 6Cu + Cr_2O_3 \\
\Delta H_{Cu_2O \rightarrow Cr_2O_3} &= \sum \Delta H_f^{products} - \sum \Delta H_f^{reactants} \\
&= \int_{298}^{T} Cp dT = -633.9 \text{ kJ}
\end{align*}
\]

The heat of formation of each reactants and product are listed in Table 3. We have assumed that the reaction was completed under adiabatic condition; the adiabatic temperature, \(T_{ad}\), due to the reaction (r1) above is estimated to be 2300 K by solving the above equation for the temperature. The heat capacities of the phases involved are listed below.

\[
\begin{align*}
Cp^{Al_2O_3} &= 117.49 + 10.3T^{-2} \text{ (J/k)} \\
Cp^{Cr_2O_3} &= 119.37 + 9.3 \times 10^{-3}T - 15.65 \times 10^5 T^{-2} \text{ (J/k)} \\
Cp^{Cu} &= 22.64 + 6.28 \times 10^{-3} T \text{ (J/k)}
\end{align*}
\]

The thermodynamic calculation was also done for the reaction (2), (3), and (4), respectively; the adiabatic temperatures for each reaction (1-4) are presented in Table 1. The estimated adiabatic temperature of the reaction (3, 4) drops significantly by adding extra Cu powder for the heat sink effect of the inert element (Cu).

Moreover, reducing the chance of direct contact for the reactants by the addition of Cu powders would give a rise to the delay of incubation time (\(t_{ig}\)). This ‘braking’ effect seems to lead the reaction to be gradual rather than the MSR (Mechanically induced Self-sustaining Reaction) [12] or combustive reaction. The gradual milling along with a longer \(t_{ig}\) is important and effective for the formation of the fine oxide dispersoids during milling [12]. The result of micro hardness test shows that the milled Cu-4Cr\(_2\)O\(_3\) powder is even harder than Cu-4Al\(_2\)O\(_3\); this is a consequence of the delayed ignition milling time of the reaction (3) in this work. This explanation well agrees with the discussion of the previous report on the suppression of MSR for the gradual reaction of the Ferro-oxide and Aluminum [8]. The experimental data of the incubation time (\(t_{ig}\)) is presented in

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**Table 3: Heat of formation (\(-\Delta H_f\)) of oxides per a mole and an oxygen in order of decreasing [12].**

| Oxide   | Heat of formation per mole, (\(-\Delta H_f, \text{kJ}\)) | Heat of formation per oxygen, (\(-\Delta H_f, \text{kJ}\)) |
|---------|---------------------------------------------------------|----------------------------------------------------------|
| Al\(_2\)O\(_3\) | 1675.7                                                   | 558.6                                                     |
| Cr\(_2\)O\(_3\) | 1139.7                                                   | 377.9                                                     |
| Cu\(_2\)O | 173.2                                                    | 173.2                                                     |
Table 1; the $t_{ig}$ of the reaction (3) is much longer than that of the reaction (4).

Takacs also reported that a displacement reaction of oxides with a higher negative enthalpy of formation ($\Delta H_f$) would be more favored [12]. The general equation representing an oxide-metal displace reaction is:

$$A_2O + yB \rightarrow xA + B_yO$$

The reaction would be thermodynamically favored in the right direction as the arrow indicates, if the heat of formation per oxygen atom is larger for the oxide of B than for the oxide of A. The Table 3 shows that the reducing metal Al (B) or Cr (B) is well above Cu (A) on the list to order to make the reaction exothermic. When the reactions (3) or (4) take place, Al is more exothermic than Cr to reduce Cu$_2$O; the formation of Al$_2$O$_3$ is more favored than that of Cr$_2$O$_3$. The heat of formation of Al$_2$O$_3$ per an oxygen is more negative than Cr$_2$O$_3$; the difference ($\sim$385.4 kJ/mol) in the heat of reaction between Al$_2$O$_3$ and Cu$_2$O is much larger than that ($\sim$204.7 kJ/mol) between Cr$_2$O$_3$ and Cu$_2$O. This data is also supporting the reason why it takes 16 h to the completion of milling for the Cu-4Cr$_2$O$_3$ whereas it does 8 h for Cu-4Al$_2$O$_3$. The corresponding XRD results for the formation of the Cr$_2$O$_3$ and Al$_2$O$_3$ can be found in this work (Figure 1) and the previous reports, respectively [7]. However, it seems that the heat of reaction ($\sim$385.4 kJ/mol) does not fairly explain why any significant difference was made between the dispersoid size of Cr$_2$O$_3$ and Al$_2$O$_3$ during the milling of powders. This may be a result of the addition of Cu and use of LN$_2$ to suppress the MSR; they could overshadow the effect of the thermodynamic parameter difference above. The suppression effect of inert addition element (Cu) and LN$_2$ in the displacement reaction of milling was discussed elsewhere [6, 8, 10, 12].

While the fine dispersoid size of Cr$_2$O$_3$ and Al$_2$O$_3$ was sustained during the milling of powders, the Cr$_2$O$_3$ dispersoid coarsened at high temperature consolidation for HP. The average radius of the dispersoids, estimated from STEM-HAADF micrographs of HPed Cu-4Cr$_2$O$_3$ in Figure 7 and Table 2, are obviously indicating that the dispersoid size of the Cu-4Cr$_2$O$_3$ are larger than the Cu-4Al$_2$O$_3$ [7]. As a result, hardness value of the HPed materials dropped to 135 (VHN, Vickers hardness number) from 270 VHN for the milled powder. This would be a result of dispersoid coarsening while hot consolidation by HP. The coarsening rate of a constant volume fraction of particle is described by the Lifshitz-Slyozov-Wagner (LSW) equation for the case when solute diffusion through the bulk materials is the controlling process [14]:

$$(\Delta r)^3 = 8k\gamma CVDt/9RT$$

where $\Delta r$ is the change in particle radius during annealing at the temperature ($T$) for the time ($t$), $k$ is a constant, $\gamma$ is the particle-matrix interface energy, $C$ is the solubility limit, $V$ is the molar volume of particle, $D$ is the diffusivity, and $R$ is the gas constant, respectively. The high resistance of oxide dispersoids to coarsening was explained in terms of the low solubility and low diffusivity of the oxide forming metallic elements in the dispersoids [2]. These two parameters are the major factors in the LSW theory as the growth of larger particles is at the expense of dissolution of smaller particles for Gibbs-Thomson effect [16]. From the thermodynamic data in the literature [1], the diffusivity and solubility of Cr and Al in copper at 1300 K can be found as follows: $D_{Al}$ (diffusivity in Cu) = 1.04 × $10^{-8}$ (cm$^2$ s$^{-1}$), $C_{Al}$ (solubility of Al in Cu) = 16.2 (at. %), $D_{Cr}$ (diffusivity of Cr in Cu) = 4.9 × $10^{-9}$ (cm$^2$ s$^{-1}$), and $C_{Cr}$ (solubility in Cu) = 0.45 (at. %).

Considering only the slower diffusivity and the lower solubility of Cr than Al in Cu for the simple estimation, we presumed that the coarsening rate of Cr$_2$O$_3$ should be lower than that of Al$_2$O$_3$. However, the result of TEM observation showed in opposite result; the rate seems not to follow the expectation of LSW theory. The similar observation can be found in other reports where the high coarsening behavior of Cr$_2$O$_3$ dispersoids ended up with the globular dispersoids of even 2-5 μm in size after internal oxidation processing at 1176-1325 K. As a consequence, the low Vickers hardness number from 90-140 (HV) depending on the percent of Cr oxide was observed. The other results likewise reveal that the Cr$_2$O$_3$ does not lead to the effective strengthening effect for its coarsening nature after hot consolidation [4, 5, 15]. It is noticeable here that the Al$_2$O$_3$ dispersoids remains small, even after recrystallization of the matrix takes place [6, 7, 9, 17]. No quantitative analysis to the individual contribution of the parameters such as the particle-matrix interfacial energy ($\gamma$) and the molar volume of particle (V) was yet made in this paper for the lack of thermodynamic data. Additional works on this topic are necessary for a deep understanding of the coarsening mechanisms of the Cr oxide dispersoids in the milled Cu matrix with the non-equilibrium microstructure of nc-Cu.
4 Conclusions

The Cr$_2$O$_3$ dispersed Cu was successfully produced by cryogenic-reactive milling and consolidated by vacuum HP at 1123K. The results of the XRD patterns as a function of milling time evidently show the formation of Cr$_2$O$_3$ dispersoids in Cu matrix at the expense of Cu$_2$O. The TEM micrographs of the milled powder reveal a mixture of the Cu matrix with nano-sized Cr$_2$O$_3$ dispersoids with a good distribution of each phases.

Thermodynamic calculation, to estimate the adiabatic temperature of the reaction by the milling, are attempted. It suggests that the formation of the Cr$_2$O$_3$ is exposed to the lower adiabatic temperature of the reaction ($T_{ad}$), longer the incubation time to ignition of the MSR (t$_{ig}$), and the smaller negative heat of formation ($\Delta H_f$), comparing to the formation of Al$_2$O$_3$ dispersoids in Cu matrix by the milling.

The delayed formation of Cr$_2$O$_3$ dispersoids results in the fine size distribution equivalent to the size distribution of Al$_2$O$_3$; the fine distribution give rise to the high hardness of Cu-4Cr$_2$O$_3$ in the milled powder. However, the hardness value of the Cu-4Cr$_2$O$_3$ drops remarkably after HP at 1123K for 2h, which is attributed to a result from the coarsening of the dispersoid. It seems that the coarsening rate of Cr$_2$O$_3$ does not obey the Lifshitz-Slyozov-Wagner (LSW) equation at the processing temperature.

References

[1] Groza, J. R. Heat-resistant dispersion-strengthened copper alloys. *Journal of Materials Engineering and Performance*, Vol. 1, No. 1, 1992, pp. 113–121.
[2] Groza, J. R., and J. C. Gibeling. Principles of particle selection for dispersion-strengthened copper. *Materials Science and Engineering A*, Vol. 171, No. 1-2, 1993, pp. 115–125.
[3] Shou, D., H. Geng, and W. Zeng, D. Zheng, H. Pan, C. Kong, P. Monroe, G. Sha, C. Suryanarayana, D. Zhang. *Materials Science and Engineering A*, Vol. 712, 2018, p. 80.
[4] Liang, S., L. Fang, and Z. Fan. Internal oxidation of Cr in Cu−Cr/Cu20 composite powder prepared by mechanical activation. *Materials Science and Engineering A*, Vol. 374, No. 1-2, 2004, pp. 27–33.
[5] Shojaeepour, F., P. Abachi, K. Purazrang, and A. H. Moghanian. Production and properties of Cu/Cr203 nano-composites. *Powder Technology*, Vol. 222, 2012, pp. 80–84.
[6] Seung, J. Hwang and J. H. Lee. Mechanosynthesis of Cu−Al$_2$O$_3$ nanocomposites. *Materials Science and Engineering A*, Vol. 405, No. 1-2, 2005, pp. 140-166.
[7] Seung, J. Hwang. Compressive yield strength of the nanocrystalline Cu with Al$_2$O$_3$ dispersoid. *Journal of Alloys and Compounds*, Vol. 509, No. 5, 2011, pp. 2355-2359.
[8] Seung, J. Hwang. Synthesis of aluminum oxide dispersed α-Fe with nano sized grains by simple milling. *Journal of Alloys and Compounds*, Vol. 638, 2015, pp. 136-140.
[9] Hahn, S. I. and Seung, J. Hwang. Estimate of the Hall-Petch and Orowan effects in the nanocrystalline Cu with Al203 dispersoid. *Journal of Alloys and Compounds*, Vol. 483, No. 1-2, 2009, pp. 207-208.
[10] Lee, J. H. and Seung, J. Hwang. Mechanosynthesis of nanocrystalline Cu with Al$_2$O$_3$ dispersoid by cryogenic milling. *Reviews on Advanced Materials Science*, Vol. 18, 2008, pp. 289-292.
[11] Ma, M., X. Liu, S. Xi, D. Chai, and J. Zhou. Effect of material characteristics on the ignition of the combustion reactions induced by ball milling. *Journal of Materials Processing Technology*, Vol. 116, No. 2-3, 2001, pp. 124-127.
[12] Takacs, L. Self-sustaining reactions induced by ball milling. *Progress in Materials Science*, Vol. 47, No. 4, 2002, pp. 355–414.
[13] Mulas, G., M. Monagheddu, S. Doppiu, G. Cocco, F. Maglia, and U. A. Tamburini. Metal–metal oxides prepared by MSR and SHS techniques. *Solid State Ionics*, Vol. 141-142, 2001, pp. 649–656.
[14] Lifshitz, I. M., and V. V. Slyozov. The kinetics of precipitation from supersaturated solid solutions. *Journal of Physics and Chemistry of Solids*, Vol. 19, No. 1-2, 1961, pp. 35–50.
[15] Patra, S., Gouthama, and K. Mondal. Densification behavior of mechanically milled Cu−8 at% Cr alloy and its mechanical and electrical properties. *Progress in Natural Science: Materials International*, Vol. 24, 2014, p. 608.
[16] Porter, D. A. and K. E. Easterling. Phase Transformations in Metals and Alloys. 2nd edn, Nelson Thornes, 2001.
[17] Stephen, J. R., R. J. Bourcier, F. J. Vigil, and D. T. Schmale. Mechanical Properties of Dispersion Strengthened Copper: A comparison of Brazing Cycle Annealed and Coarse Grain Microstructures. SANDIA Report, SAND88-1351, 1988.