



## Review Article

# A review of microstructure and texture evolution with nanoscale precipitates for copper alloys



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## ABSTRACT

Copper alloys are widely used in the lead frame, high-speed railway and other applications due to their high electrical conductivity and adequate mechanical properties. In this work, the texture and microstructure evolution under hot deformation of Cu-Ni-Si, Cu-Co-Si and Cu-Fe-P alloys were investigated. In order to analyze the texture evolution, the standard pole figures and ODF figures were established. The TEM analysis shows that the addition of trace elements promoted the dispersion of nanoscale precipitated phase particles in the matrix, which can hinder the movement of grain boundaries and dislocations. In addition, the suitable hot processing parameters for the Cu-Fe-P alloy were determined from the hot working diagram. Finally, the comprehensive diagrams for the effects of addition of the alloying elements on the electrical conductivity and ultimate tensile strength of the Cu-Ni-Si and Cu-Fe-P alloys were obtained.

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## 1. Introduction

Copper alloys are favored due to their high conductivity and excellent mechanical properties [1–7], and are widely used in aerospace, high-speed railway, home appliances, lead frames

and so on [8–13]. The application diagram of copper alloys is shown in Fig. 1. Typical characteristics of pure copper are high conductivity, excellent ductility and low strength, which narrows its applications [14]. In order to improve the mechanical properties of the copper, many researchers tried adding alloying elements, such as Co [10,15,16], Al [17–19], Mg [20–22],

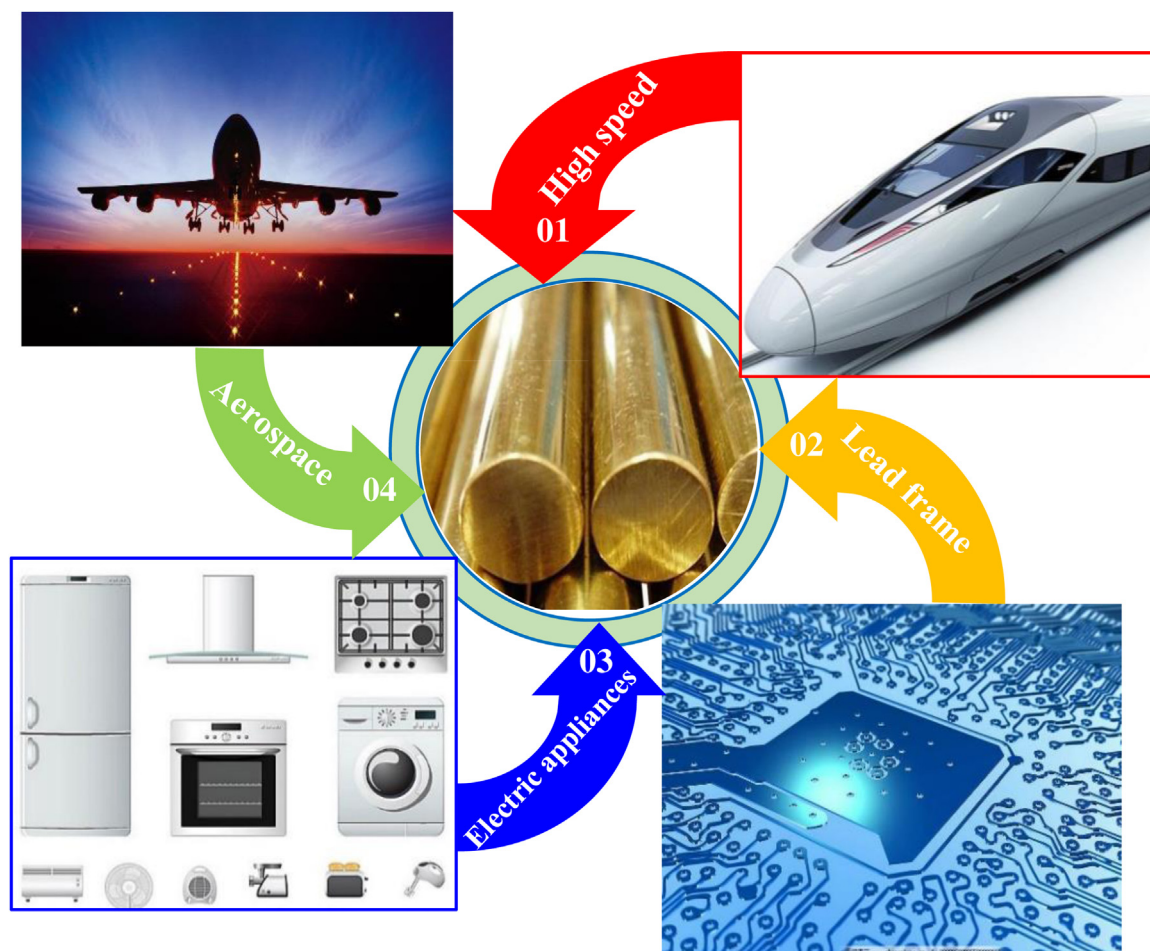
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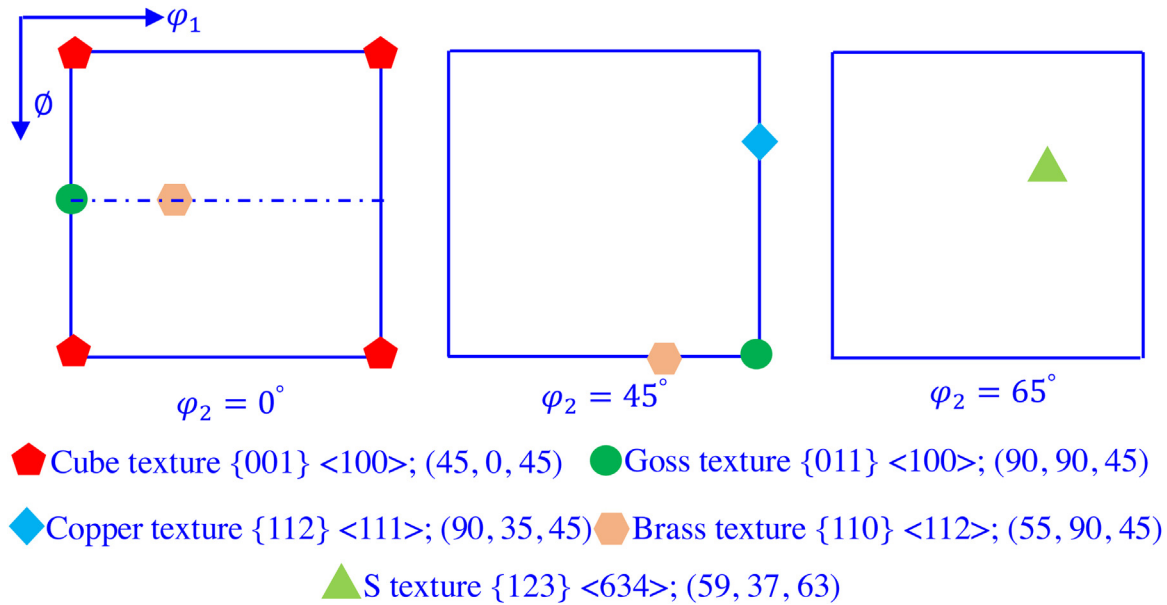


**Fig. 1 – The application diagram of copper alloys.**

Fe [23–25], Ti [26–29], Ag [30–32], Cr [33–35], Zr [36–38]. Good results have been achieved, demonstrating that the addition of trace alloy elements can refine grains, delay the recrystallization process, and improve the strength and hardness of copper alloys. In the past few decades, commonly used copper alloys include Cu-Ni-Si [39,40], Cu-Ni-Al [41,42], Cu-Cr-Zr [43,44], Cu-Mg [45,46] and so on. Ni and Si can form  $\text{Ni}_2\text{Si}$  intermetallic compounds in copper alloys, and the solubility of  $\text{Ni}_2\text{Si}$  in copper matrix decreases sharply with the decrease of temperature, which has a strong precipitation strengthening effect. Ni and Al can form NiAl or  $\text{Ni}_2\text{Al}$  in copper alloys, which have strong precipitation strengthening effects at 450–600 °C. The addition of Cr and Zr produces the intermetallic compounds, which improve the strength, heat resistance and electrical conductivity of copper alloys. Lei et al. [47] obtained a high strength of Cu-Ni-Si alloy by the combined cold rolling and aging process with a peak aging performance of 381 HV (hardness), 1155.8 MPa (ultimate strength), 3.5% (elongation), and 25.2% IACS (electrical conductivity). Chalon et al. [48] investigated the flow stress, work-hardening and work-softening behavior of the Cu-Ni-Si alloy deformed at 600–950 °C. The hot working of this alloy should be carried out at temperatures higher than 850 °C, so as to obtain full benefits from the grain refinement effect due to DRX (dynamic recrystallization). Fu et al. [49] investigated the transforma-

tion of microstructure and properties in Cu-Cr-Zr alloy during cold deformation and aging processes. The results showed that plasticity is closely related to texture transformation and precipitation of large amount of Cr particles, increasing the electrical conductivity and strength. Shen et al. [50] developed a new process of hot rolling and intermediate annealing with high strength and electrical conductivity in Cu-Cr-Zr alloy. High strength and conductivity may be attributed to the fine grains and rapid precipitation of secondary phases. With the rapid development of the technology and modern economy, higher performance requirements of copper alloy are put forward, especially for those used for lead frames and high-speed railways. Therefore, researchers have been trying to add rare earth elements, such as Ce [51,52] and Y [53,54], to improve the copper alloys properties. Wang et al. [46,51] investigated the hot deformation behavior of Cu-Mg alloy with Ce and Y addition. The addition of Ce and Y significantly increased the flow stress, and activation energy for hot deformation, while it inhibited the dynamic recrystallization of the alloy, attributed to promoting precipitation and increasing number of twins after deformation.

The processing technology of copper alloys mainly includes hot deformation and aging after cold deformation. Hot deformation is a basic component of heat treatment and is widely used to investigate the hot working properties of copper



**Fig. 2 – Schematic illustration of the ideal texture components for copper alloy, ODF maps at  $\varphi_2 = 0^\circ$ ,  $45^\circ$  and  $65^\circ$ .**

alloys. Generally speaking, the hot deformation temperature and deformation rate are the main parameters that affect the hot deformation behavior of the copper alloys. Studying microstructure transformations, thermal activation energy and hot processing maps can be used to obtain the optimal deformation parameters for the hot working performance of copper alloys. Especially for the electron backscatter diffraction (EBSD) analysis obtained by the JSM-7800F backscatter scanning electron microscope, it plays a more and more important role in the analysis of hot deformation, which can be used to analyze the microstructure and orientation of solid crystal materials under various processing conditions. In face-centered cubic (FCC) materials, the deformation process is usually accompanied by the development of unique microstructure and significant crystal texture. Especially, the development of texture during deformation is very important to control the anisotropy of mechanical properties, so it is necessary to understand the texture correctly [55]. Due to the varying orientations of grains in polycrystalline metals, the occurrence time and number of slip in grains are different, the strength of interaction between dislocations is also different, the distribution of orientation difference in crystal is certain to be different, and the deformation structure is also different. Therefore, the polycrystalline metals deformation should be inhomogeneous, and this difference has different effects on the subsequent dynamic recrystallization or phase transformation, which can be easily detected by EBSD. Moreover, the texture transformation is closely related to the properties of the alloys after heat treatment, which can be obtained from the EBSD. For FCC Metals, the main textures include  $\{001\} \langle 100 \rangle$  cubic texture, the  $\{011\} \langle 100 \rangle$  Goss texture,  $\{112\} \langle 111 \rangle$  copper texture,  $\{111\} \langle 211 \rangle$  R texture and so on [56,57]. There are many factors that affect texture transformation during deformation, such as processing parameters and material parameters [58]. Among them, the starting grain size and strain path are the two important process parameters that

have a significant influence on the microstructure and texture [59]. Bhattacharjee et al. [60] investigated the effects of starting grain size ( $36 \mu\text{m}$  and  $800 \mu\text{m}$ ) on the evolution of texture in nickel during the cross-rolling process. The results show that the significant difference in the texture was much stronger Brass ( $\{011\} \langle 112 \rangle$ ) and rotated Brass ( $\{011\} \langle 744 \rangle$ ) components in the fine grained starting material compared to the coarse grained starting material. It can be attributed to the different grain refinement behavior due to the large initial grain size, which is closely related to the dispersed and fragmented structure formed in the material. The change of strain path during cold rolling has a significant effect on the evolution of deformation texture, which has the characteristic of rotating  $90^\circ$  around the normal direction (ND) between consecutive passes so that the transverse direction (TD) of the previous rolling pass becomes the rolling direction (RD) of the current rolling pass [58,59,61]. The cross rolling processes are in sharp contrast to conventional or unidirectional routes, where RD remains constant throughout the process. Cross rolling has great influence on the formation of microstructure and texture during deformation and annealing, which has been extensively investigated in FCC materials [60,62–64]. Bhattacharjee et al. [61] reported the effects of change in strain path during cold rolling on the evolution of microstructure and texture. It was found that the copper-type texture was observed in unidirectional processed materials, while the strong brass texture was developed during cross rolling. The important material parameter which can have a significant impact on microstructure and texture is stacking fault energy (SFE) [58,60]. Brass texture is observed with the dominant component of Brass component in low SFE materials. While pure metal or copper-type texture, which are characterized by the strong Cu, S, and Brass components, can be observed in high to medium SFE materials, such as Ni and Cu [61,65]. It is especially pointed out that the addition of alloying elements will reduce the SFE of copper alloys [66]. Moreover, the addition of alloying elements

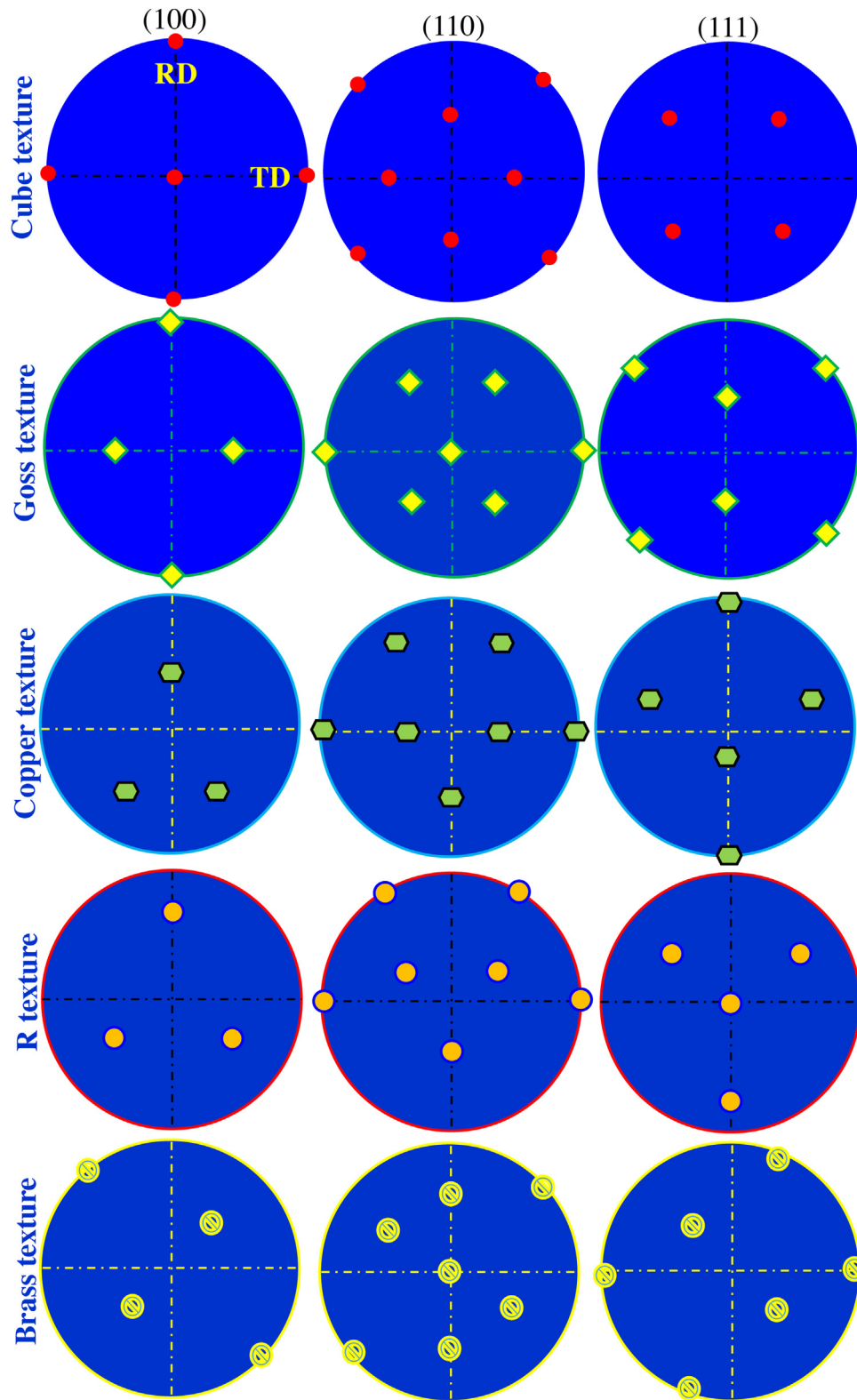
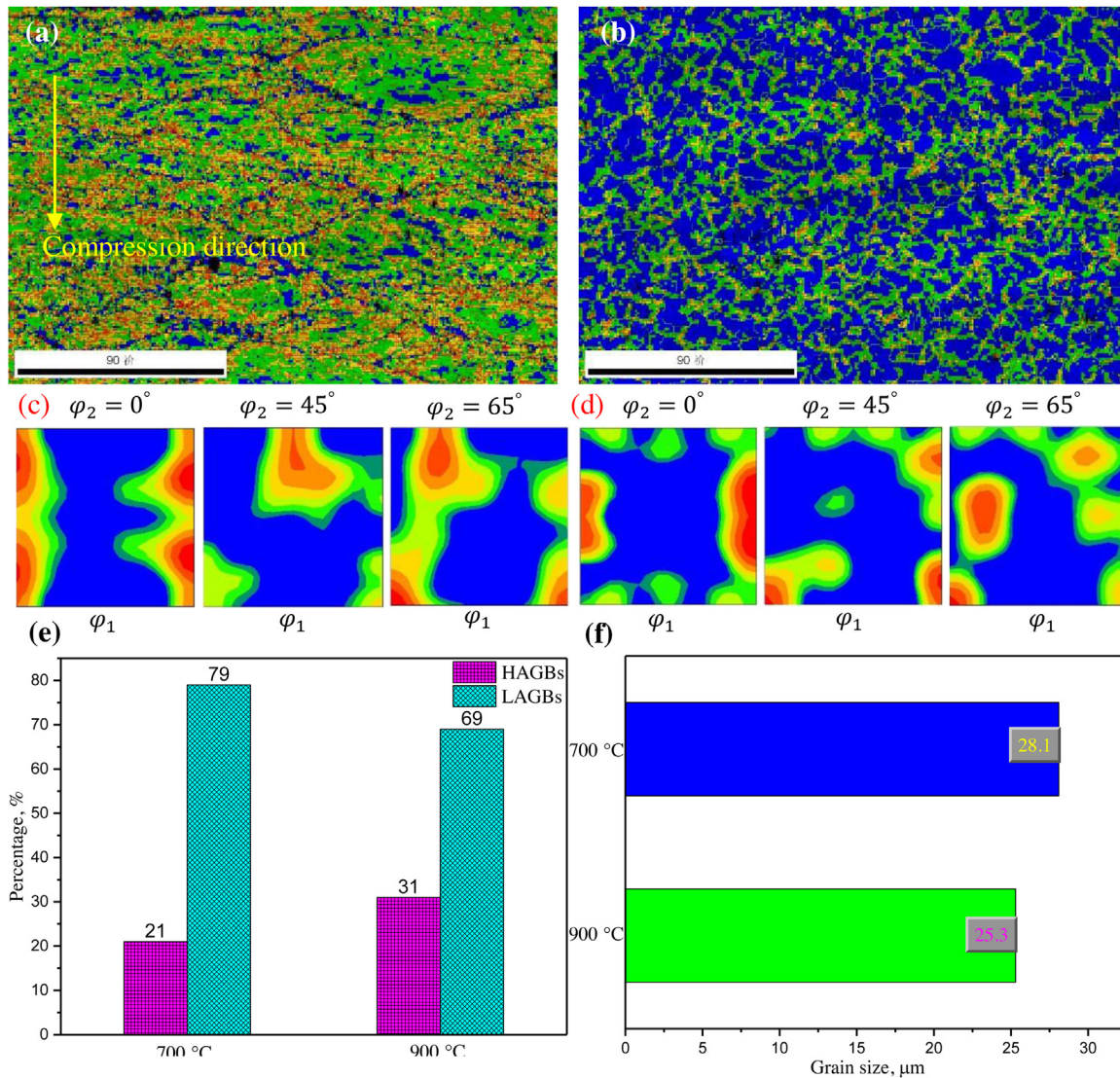


Fig. 3 – Schematic illustration of the ideal texture components for copper alloy at (100), (110) and (111) standard pole figures.

has a certain influence on the deformation and recrystallization texture. For example, it is known to significantly affect strength of the recrystallization texture in high to medium SFE materials. The results analyzed by Ray and Bhattacharjee

[67] indicated that the W and Mo addition developed a much sharper cube texture compared with pure Ni. Besides, W and Mo enhance the cube texture intensity in Ni by decreasing the volume fraction of the rotated cube grains.





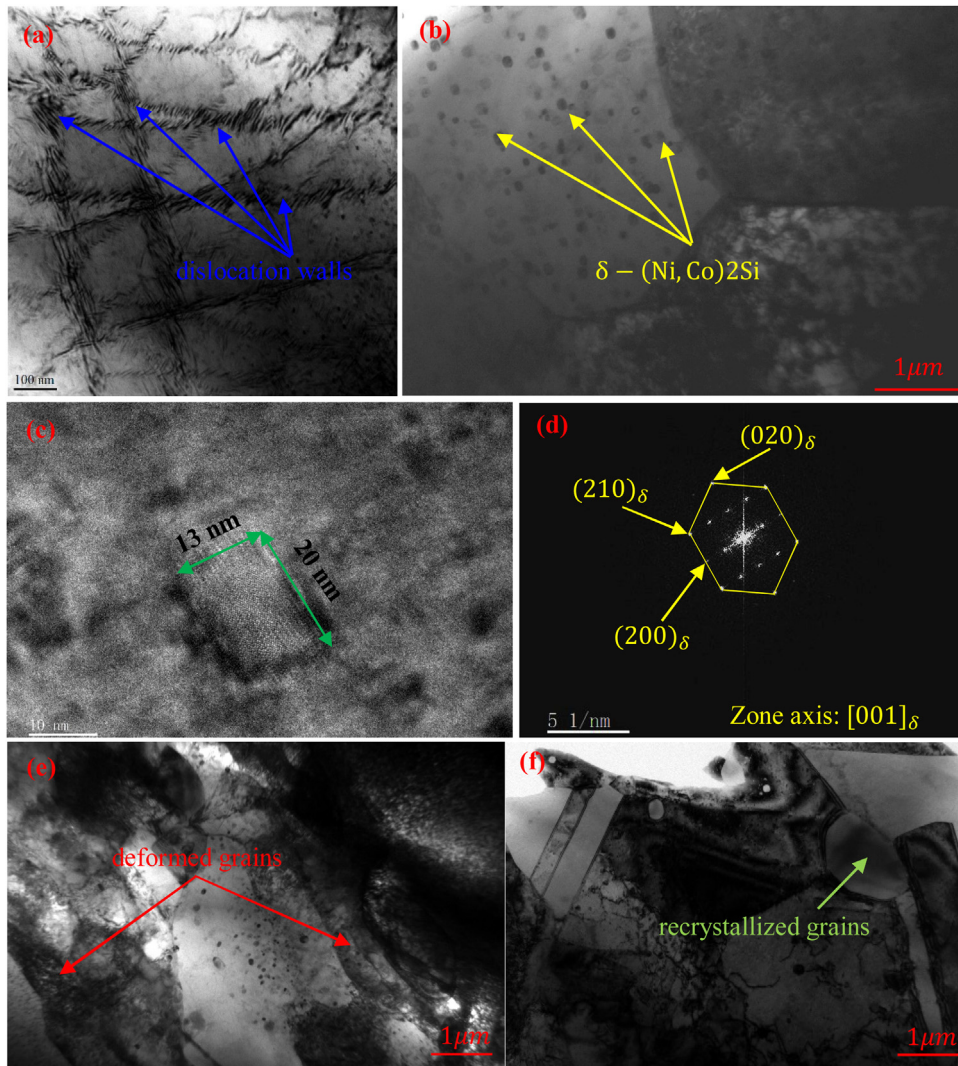
**Fig. 4 – EBSD maps of Cu-Ni-Si alloy: (a) KAM map deformed at  $0.01 \text{ s}^{-1}$  and  $700 \text{ }^\circ\text{C}$ ; (b) KAM map deformed at  $0.01 \text{ s}^{-1}$  and  $900 \text{ }^\circ\text{C}$ ; (c) ODF map of (a); (d) ODF map of (b); (e) HAGBs and LAGBs percentage deformed at  $700 \text{ }^\circ\text{C}$  and  $900 \text{ }^\circ\text{C}$ ; (f) corresponding average grain size deformed at  $700 \text{ }^\circ\text{C}$  and  $900 \text{ }^\circ\text{C}$ .**

The cold deformation, aging temperature and time are direct factors that affecting the properties of age-strengthened copper alloys. The nanoscale precipitates in the aging process result in the high conductivity and strength of copper alloys. The combined process of cold deformation and aging for copper alloys with a small amount of alloying elements can greatly improve the hardness and tensile properties of the copper alloy due to the high dislocation density and fine precipitates, although the conductivity is slightly sacrificed. Therefore, understanding and optimizing the aging process is an important factor to control the precipitation of secondary phases to improve the properties of copper alloys [68]. In this work, several typical copper alloys (Cu-Ni-Si, Cu-Co-Si, and Cu-Fe-P) were analyzed, especially for the EBSD analysis, microstructure evolution and nanoscale precipitates.

## 2. Cu-Ni-Si alloy

Although Cu-Be alloy has high conductivity ( $\sim 22\%$ IACS) and strength ( $\sim 1000 \text{ MPa}$ ), it has been almost replaced by the Cu-Ni-Si alloy in recent decades due to its harmful effect on human health [47,69–71]. A large amount of research reports show that when the content of Ni and Si is high, the alloy has high strength but low conductivity, which can be used as elastic conductive spring and other elastic conductive materials [72–75]. When the content of Ni and Si is low, the copper alloys have high conductivity and strength, and can be used as the lead frame materials [76–81].

The microstructure transformation during hot deformation is an important index to evaluate the hot working properties and dynamic recrystallization characteristics. In



**Fig. 5 – TEM micrographs of Cu-Ni-Si alloy deformed at  $0.01 \text{ s}^{-1}$  and  $700 \text{ }^\circ\text{C}$ : (a), (b), (e) and (f) bright field images; (c) HRTEM of (b); (d) FFT of (c).**

addition, the texture is closely related to the hot working properties of the copper alloy. Fig. 2 shows a schematic illustration of the ideal texture components for copper alloy according to the ODF maps at  $\varphi_2 = 0^\circ$ ,  $45^\circ$  and  $65^\circ$  and the Euler angles of corresponding texture. In addition, Fig. 3 shows the schematic illustration of the ideal texture components for copper alloy at (100), (110) and (111) standard pole figures.

Fig. 4 shows the EBSD maps and corresponding ODF maps, misorientation angle and average grain size of the Cu-Ni-Si alloy deformed at  $0.01 \text{ s}^{-1}$  with different temperature of  $700 \text{ }^\circ\text{C}$  and  $900 \text{ }^\circ\text{C}$ . As illustrated in the Fig. 4(a), there are a lot of deformed grains and a few recrystallized grains (indexed by blue color) around the deformed grains in the structure. With the increasing of deformation temperature, the number of dynamic recrystallized grains increases significantly, the deformed grains are replaced by recrystallized grains, and the microstructure is more uniform. In addition, the average grain size decreased from  $28.1 \mu\text{m}$  to  $25.3 \mu\text{m}$ , which is attributed to the transformation of deformed grains into recrystallized grains due to the acceleration of dynamic recrystallization.

The black area in Fig. 4(a) indicates that the unindexed black area has higher lattice distortion than the indexed area [82]. It is also shown that the deformation energy at low temperature is higher than that at high temperature compared Fig. 4(a) with (b). The driving force of dynamic recrystallization is the stored energy related to dislocations during deformation, which will be released when dynamic recrystallization occurs. This can explain why the dynamic recrystallization accelerates with the increasing of temperature. In addition, the diffusion of atoms is also one of the reasons for the acceleration of dynamic recrystallization with the increasing of temperature. It can be inferred that Fig. 4(c) and (d) are the  $\{001\} \langle 100 \rangle$  cubic texture and the  $\{011\} \langle 100 \rangle$  Goss texture, respectively, by comparing the standard ODF maps in Fig. 2. Moreover, the texture tends to strengthen with the increasing of temperature. The first step of dynamic recrystallization is to form some crystal nuclei in the deformed matrix, which are surrounded by a large angle interface and have a high degree of structural integrity. The nucleus then grows by swallowing the surrounding matrix until the whole matrix is filled with



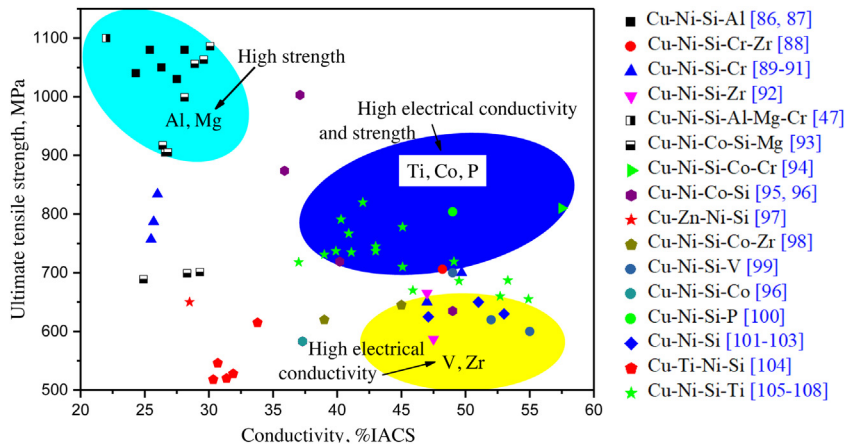


Fig. 6 – The comprehensive properties of the Cu-Ni-Si alloy with different types of alloy elements [47,86–108].

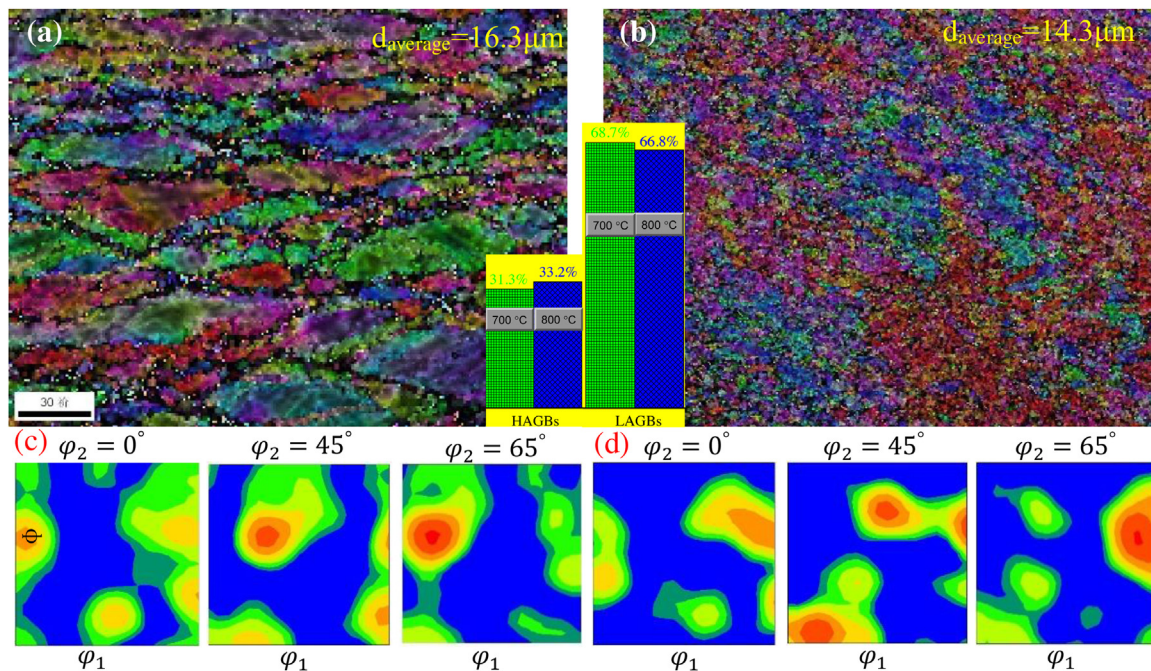
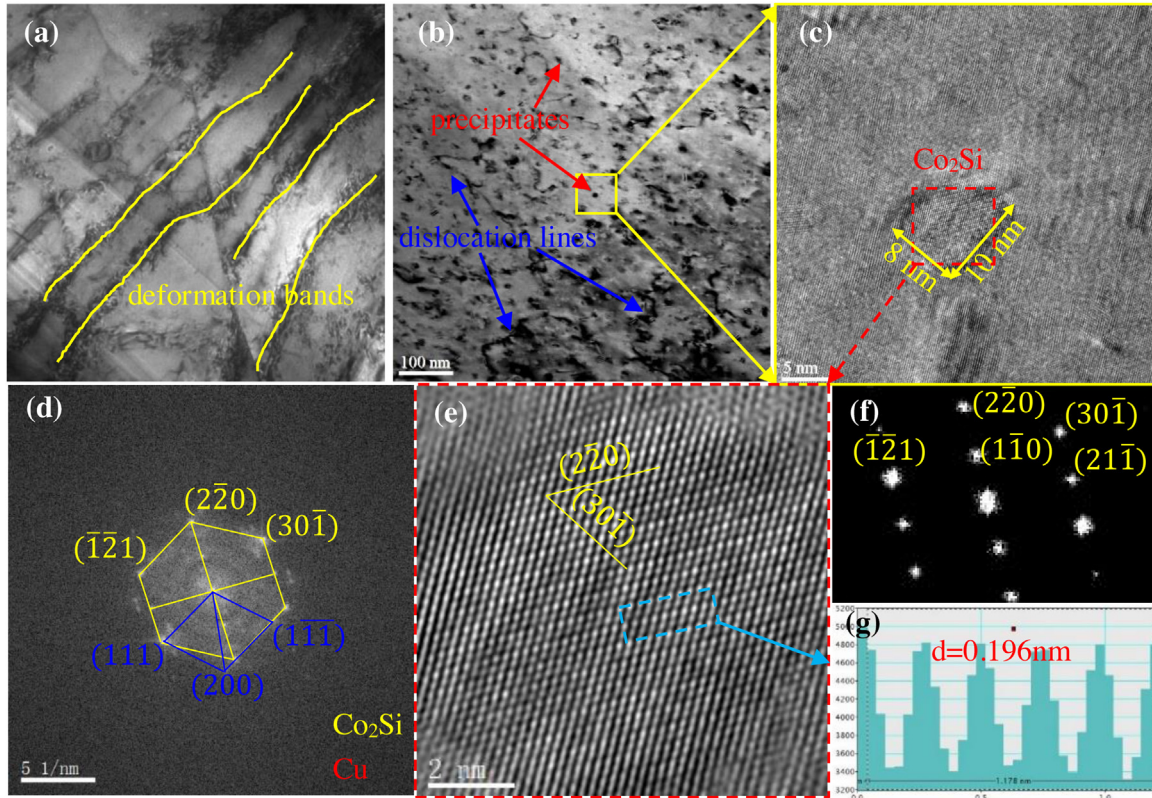


Fig. 7 – Microstructure of Cu-Co-Si-Ti alloy: (a) KAM map deformed at 700 °C and 0.01 s<sup>-1</sup>; (b) KAM map deformed at 800 °C and 0.01 s<sup>-1</sup>; (c) ODF map of (a); (d) ODF of (b);

new grains. The necessary conditions for the recrystallization nucleus is that they can engulf the surrounding matrix in the way of interface movement and form new grains of a certain size. Therefore, only the sub crystal with a large angle interface with the matrix can become a potential recrystallization nucleus. In other words, the content of dynamic recrystallization grain can be qualitatively inferred from the content of large angle grain boundary. Generally speaking, the recrystallization nucleation usually takes priority at the original grain boundaries, near the inclusion base surfaces, at the deformation zones and the edge cutting zones. As given in the Fig. 4(e), it shows the HAGBs and LAGBs of Cu-Ni-Si alloy deformed at 700 °C and 900 °C. It can be seen that the percentage content of HAGBs increases with the increasing of temperature, which

can also prove that the degree of dynamic recrystallization increases with the increasing of temperature based on the above analysis [83–85].

Fig. 5 shows the TEM micrographs of Cu-Ni-Si alloy deformed at 0.01 s<sup>-1</sup> and 700 °C. It can be seen that there are many dislocation walls and nanoscale precipitates with the size of 13 nm × 20 nm inside the grains. The existence of dislocation walls can hinder the migration of grain boundaries and make the deformation more difficult. The precipitates can be determined to be  $\delta\text{-(Ni, Co)}_2\text{Si}$  according to the diffraction pattern in Fig. 5(d). In addition, the zone axis of  $\delta\text{-(Ni, Co)}_2\text{Si}$  can be calculated as  $[001]_{\delta}$ . Ban et al. [35] investigated the effects of Cr addition on the constitutive equation and precipitated phases of copper alloy by the EBSD and TEM analysis. It can



**Fig. 8 – Microstructure of Cu-Co-Si-Ti alloy: (a), (b) TEM micrographs deformed at 700 °C and 0.01 s<sup>-1</sup>; (c) HRTEM; (d) FFT of (c); (e), (f) IFFT of (h); (g) measurement of crystal surface spacing.**

be concluded that the addition of Cr can make the precipitated phase finer and microstructure more homogeneous, and enhance the thermal deformation activation energy of the Cu-Ni-Si alloy after deformation. The constitutive equations of the two alloys are as follows:

For Cu-Ni-Co-Si alloy:

$$\dot{\epsilon} = e^{63.38} [\sinh(0.009\sigma)]^{9.04} \exp\left(-\frac{569800}{8.314T}\right)$$

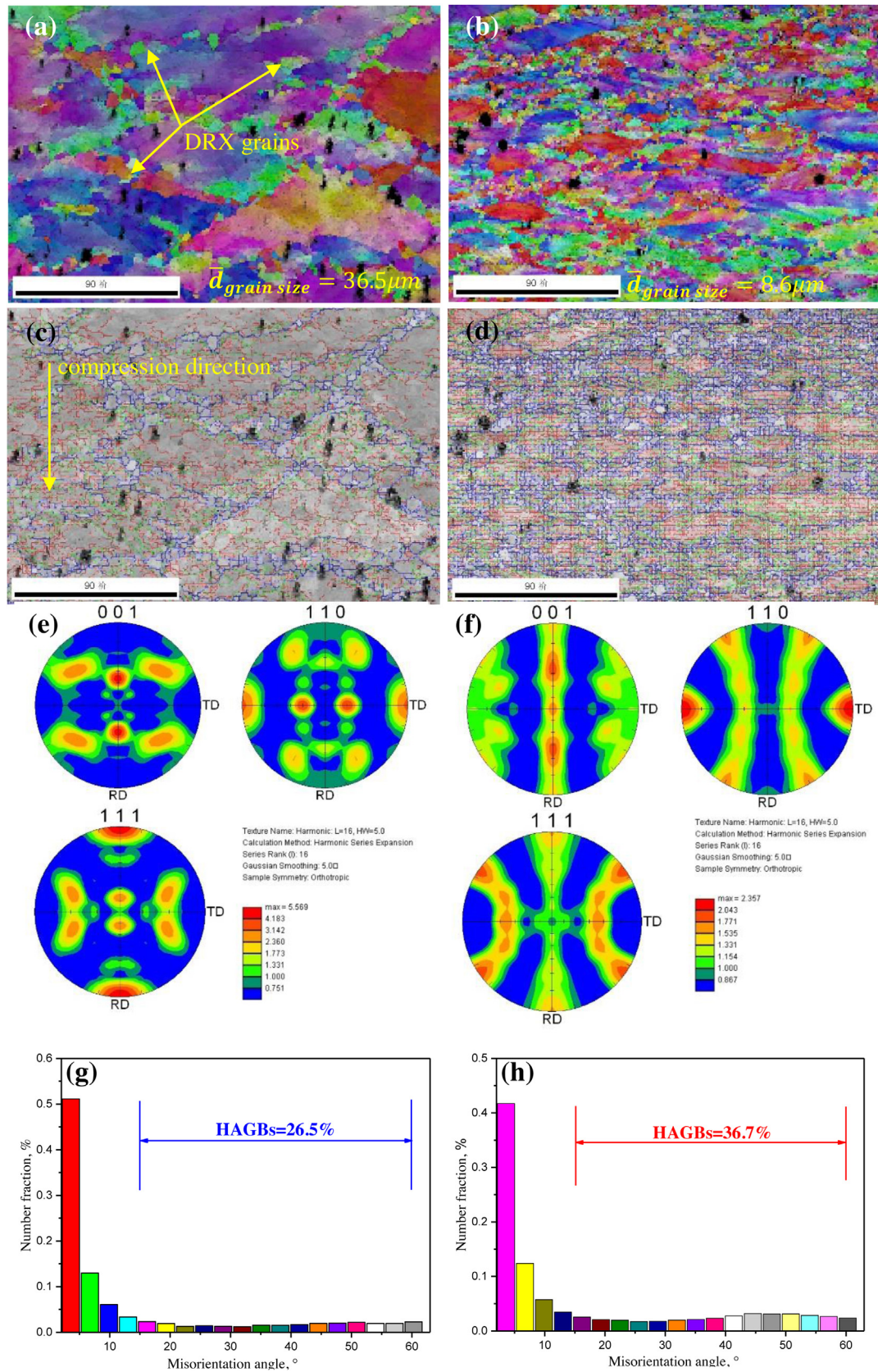
For Cu-Ni-Co-Si-Cr alloy:

$$\dot{\epsilon} = e^{75.35} [\sinh(0.005\sigma)]^{13.37} \exp\left(-\frac{639500}{8.314T}\right)$$

Fig. 6 shows the electrical conductivity and ultimate tensile strength of Cu-Ni-Si alloy with the different trace alloy elements, such as Al, Mg, Co, Cr, Ti. It can be seen that the Cu-Ni-Si alloys have high strength but low conductivity due to the addition of Al and Mg. Lei et al. [86] found that the addition of aluminum promotes precipitation, effectively refines the grains and improves the stress relaxation resistance of the alloy. After 50% cold deformation and aging at 450 °C for 60 min, the peak properties of the Cu-Ni-Si-Al alloy were obtained: the conductivity was 28.1% IACS; the micro hardness was 343 HV; and the tensile strength was 1080 MPa. The Cu-Ni-Si alloy has high conductivity and low strength due to the addition of V or Zr. However, the addition of Ti, Co and P makes the Cu-Ni-Si alloy have high conductivity and strength at the same time, i.e. good comprehensive properties. Xiao et al. [96]

got a high conductivity and strength of Cu-Ni-Si alloy by the Co addition. The results show that Co addition delayed the occurrence of Spinodal decomposition, which was explained by analyzing the microstructural observation. Zhang et al. [100] investigated the effects of P addition on microstructure and mechanical property of the Cu-Ni-Si-P alloy. After aging at 450 °C for 48 h, the semi coherent precipitates ( $\delta$ -Ni<sub>2</sub>Si) with the average size of 5 nm were observed in the microstructure by TEM analysis. At the same time, it also obtained the best comprehensive performance of 49% IACS and 804 MPa, which is attributed to the finer grains and acceleration of precipitation due to the addition of P. Ti element is more special, when the content is higher, the conductivity and strength of the alloy are relatively low. Liu et al. [104] investigated the aging strengthened Cu-3Ti-3Ni-0.5Si alloy with a high Ti content. Since the large solubility of Ti solute atoms in the Cu matrix enhances electron scattering, Cu-Ti alloys exhibit the poor electrical conductivity. Moreover, the precipitated phase particles transformed from Cu<sub>4</sub>Ti phase to equilibrium and incoherent Cu<sub>3</sub>Ti phase with aging, which greatly reduces the strength of Cu Ti alloy. However, when Ti content is low, it shows good comprehensive performance. Some researches [105–108] show that the addition of a small amount of Ti can refine grains and promote precipitation ( $\delta$ -Ni<sub>2</sub>Si), which can explain the reason of high conductivity and high strength for Cu-Ni-Si-Ti alloy. As for the addition of other alloy elements, there is no obvious characteristics.





**Fig. 9** – Microstructure of Cu-Fe-P alloy deformed at  $0.01 \text{ s}^{-1}$  with different temperature: (a) IPF map deformed at  $700 \text{ }^\circ\text{C}$ ; (b) IPF map deformed at  $800 \text{ }^\circ\text{C}$ ; (c) EBSD orientation maps of (a); (d) EBSD orientation maps of (b); (e) pole figures of (a); (f) pole figures of (b); (g) misorientation angle distribution of (a); (h) misorientation angle distribution of (b).

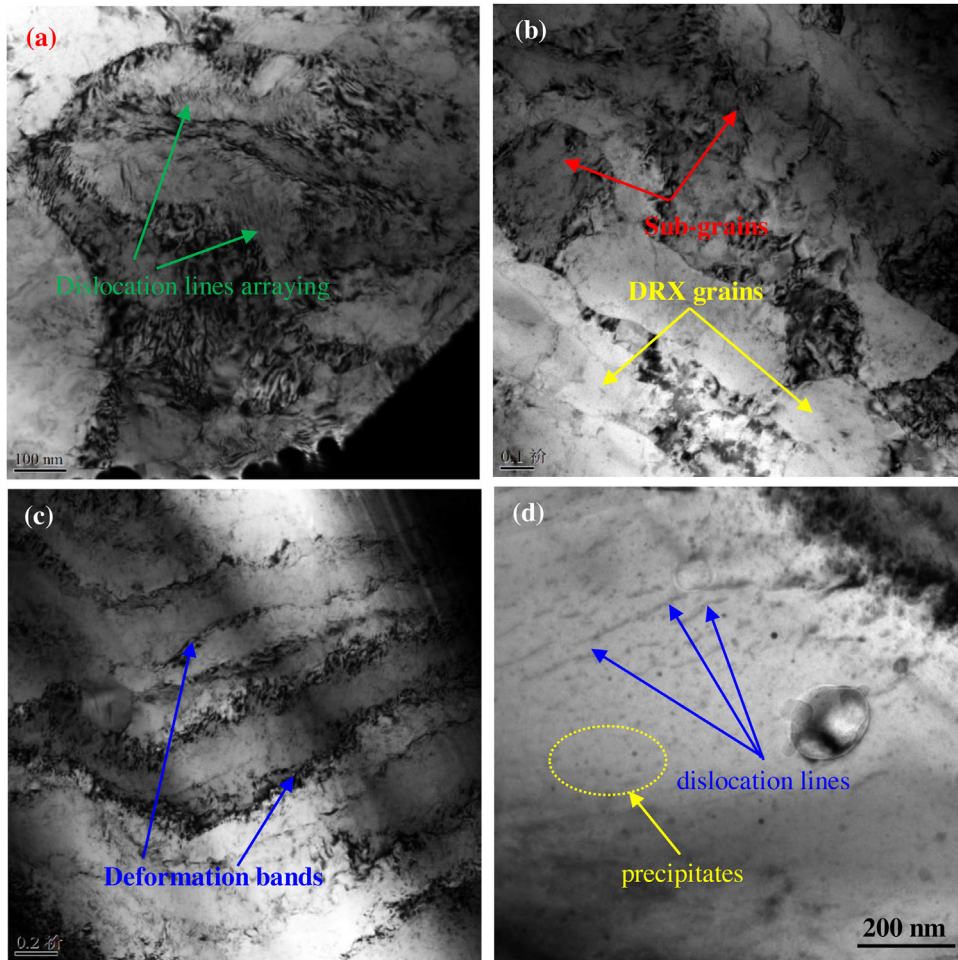


Fig. 10 – TEM micrographs of Cu-Fe-P alloy deformed at 700 °C, 0.01 s<sup>-1</sup>.

### 3. Cu-Co-Si alloy

Liu et al. [109] investigated the texture distribution and precipitates of Cu-Ni-Si alloy at the aging process. With the increasing of aging temperature, the strength of copper texture  $\{211\} \langle 111 \rangle$  and Goss texture  $\{011\} \langle 100 \rangle$  decreased, while the strength of cubic texture  $\{001\} \langle 100 \rangle$  increased, which can be attributed to the influence of precipitation ( $\text{Ni}_2\text{Si}$ ) on the surrounding deformation area and then influence the texture strength. Lei et al. [110] obtained a high strength of Cu-Ni-Si alloy by analyzing the phase transformation and properties. The results shows that there are multi-precipitation phases ( $\text{Ni}_2\text{Si}$ ,  $\gamma\text{-Ni}_3\text{Al}$ ,  $\beta\text{-Ni}_3\text{Si}$ ), which play a significant role in improving the strength of studied alloy. Zhao et al. [16] and Xiao et al. [96] investigated the effects of Co addition on the electrical conductivity and mechanical properties of Cu-Ni-Si alloy. The electrical conductivity and mechanical properties are greatly improved due to the Orowan precipitation strengthening. In recent years, a lot of researches have been carried out based on the Cu-Ni-Si alloy by adding Co element, and the results show that the properties of the alloys are improved significantly by substituting a small amount of

Co for Ni atom ( $\delta\text{-(Ni, Co)}_2\text{Si}$ ). Based on the above investigations, our team have a bold conjecture that the Co atom can completely replace the Ni atom and a small amount of Ti element is added, i.e. Cu-Co-Si-Ti alloy [29,111,112].

Fig. 7 shows the Kernel Average Misorientation (KAM) maps and corresponding ODF maps of Cu-Co-Si-Ti alloy deformed at 0.01 s<sup>-1</sup> with different temperature of 700 °C and 800 °C. It is a kind of typical necklace structure, where a few fine recrystallized grains are around the deformed grains with an average grain size of 16.3 μm. Moreover, the HAGBs and LAGBs of the studied alloy deformed at 0.01 s<sup>-1</sup> and 700 °C are 31.3% and 68.7%, respectively. With the deformed temperature increasing to 800 °C, the microstructure shows that the deformed grains are replaced by recrystallized grains and the microstructure becomes uniform. The average grain size is thus reduced to 14.3 μm. In addition, the content of HAGBs of the Cu-Co-Si-Ti alloy also increased, suggesting that the recrystallized volume fraction increases due to higher temperatures. As illustrated in Fig. 7(a), there are some unindexed regions in the Cu-Co-Si-Ti alloy under relatively low temperature deformation, which are similar to the Cu-Ni-Si alloy deformed at low temperature. Therefore, it can be inferred that there are more lattice distortion energy and dislocation



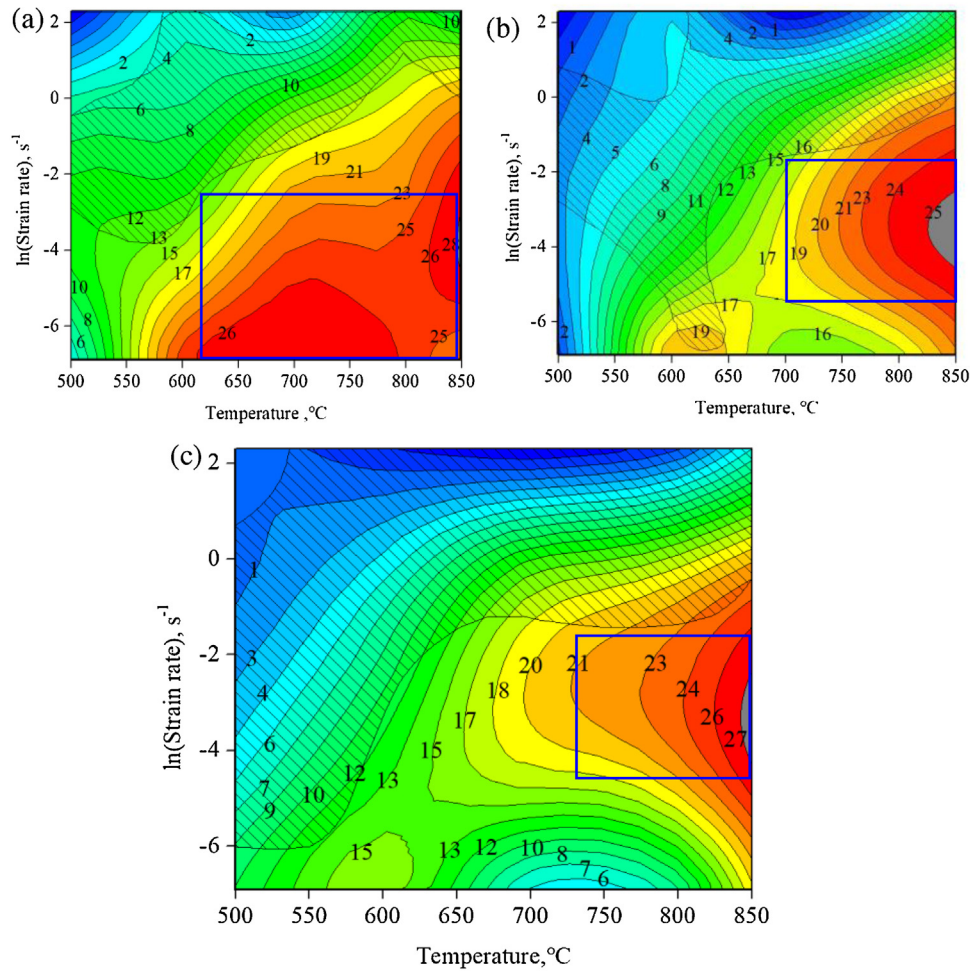


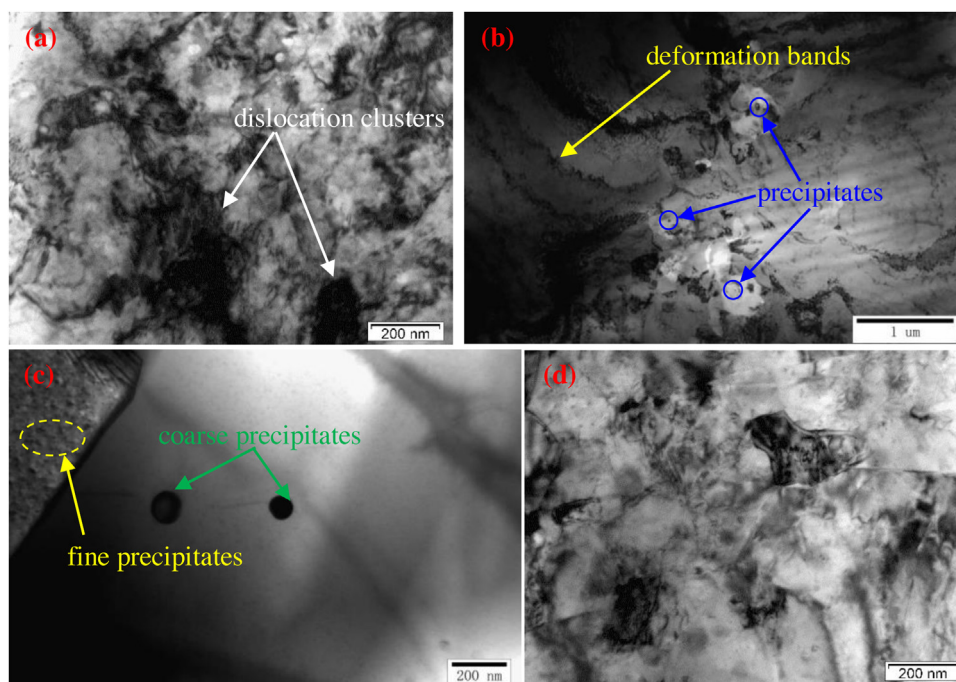
Fig. 11 – Hot processing maps of Cu-Fe-P (a), Cu-Fe-P-Ce (b) and Cu-Fe-P-Y (c) alloys.

energy around the deformed grains, which will be used for the nucleation of dynamic recrystallization grains [113,114]. As for the texture transformation of Cu-Co-Si-Ti alloy shown in the Fig. 7(c) and (d), it can be known that there are the {011} <100> Goss texture and {112} <111> copper texture deformed at 700 °C and 800 °C, respectively, by comparing the standard ODF maps in Fig. 2.

Fig. 8 shows the microstructure of Cu-Co-Si-Ti alloy deformed at 0.01 s<sup>-1</sup> and 700 °C. As given in Fig. 8(a), there are some deformation bands in the microstructure, which can hinder the migration of grain boundaries and the movement of dislocations [115]. In addition, there are a lot of fine precipitates inside the grains, and some precipitates are surrounded by dislocation lines in Fig. 8(b). Fig. 8(c) shows the HRTEM image of the precipitates with the size of 8 nm × 10 nm in Fig. 8(b). It can be determined to be the Co<sub>2</sub>Si with the lattice parameters of a = 7.109 nm, b = 4.918 nm and c = 3.737 nm by the diffraction pattern in Fig. 8(d). And the zone axis of Cu and Co<sub>2</sub>Si is [011]<sub>Cu</sub> and [113]<sub>Co<sub>2</sub>Si</sub>, respectively. Moreover, the directions of the (220) and (301) for the Co<sub>2</sub>Si can be determined according to Fig. 8(d). Finally, the crystal surface spacing of the Co<sub>2</sub>Si is 0.196 nm.

#### 4. Cu-Fe-P alloy

Cu-Fe-P alloy is usually used as electronic components, such as semiconductor lead frame and electrical connector due to its high conductivity and medium strength [116,117]. The solubility of Fe in copper can reach 3.5% at 1050 °C while 0.15% at 635 °C. The addition of Fe has some benefits, such as refining the grains, delaying the recrystallization process and improving the mechanical properties of the copper alloy, although it will reduce the electrical conductivity and thermal conductivity of copper. The maximum solubility of P in copper matrix is 1.75%, which is almost 0% at the room temperature. In addition, P has a good effect on the mechanical properties and welding properties of copper alloys. Cao et al. [118] investigated the stability of the fine-grained microstructure of Cu-Fe-P alloy by the isothermal annealing. The results shows that the appearance of Fe<sub>3</sub>P phase can refine the grains and improve the stability of microstructure, which was uniformly distributed in the grain interior and grain boundaries. Wang et al. [119] investigated the nanoscale precipitates evolution of Cu-Fe-P-Mg alloy by the aging treatment. And it can be inferred



**Fig. 12 – TEM micrographs of Cu-Fe-P alloy aging at 460 °C for 20 min.**

that the precipitation of  $Mg_3P_2$  phase inhibited the precipitation of  $Fe_3P$  particles, therefore, the alloy obtained an excellent comprehensive property of 599 MPa and 71.1%IACS.

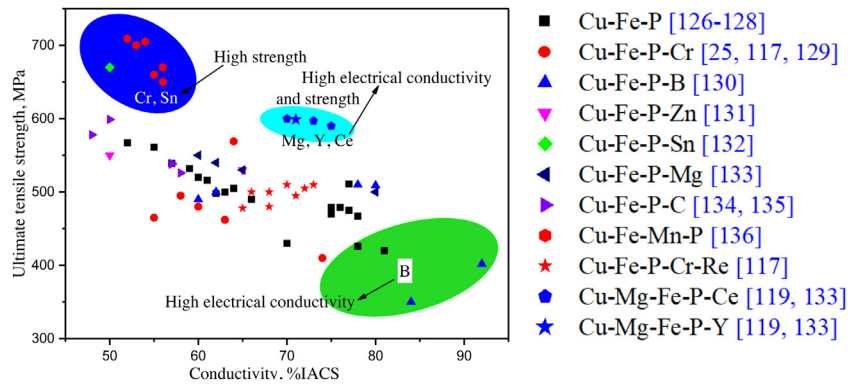
Fig. 9 shows the microstructure evolution of Cu-Fe-P alloy deformed at  $0.01\text{ s}^{-1}$  strain rate with different temperature. As shown in the Fig. 9(a) and (c), the recrystallized grains near the deformed grains have grown to an average size of  $36.5\text{ }\mu\text{m}$ . With the temperature increasing to  $800\text{ }^\circ\text{C}$ , the recrystallized grains have grown at low temperature, and the deformed grains have recrystallized with average size of  $8.6\text{ }\mu\text{m}$ . In addition, the texture of Cu-Fe-P alloy deformed at  $700\text{ }^\circ\text{C}$  and  $800\text{ }^\circ\text{C}$  can be determined as the  $\{112\}\langle 111\rangle$  copper texture and  $\{111\}\langle 211\rangle$ R texture, respectively, by the standard pole figures in Fig. 3, which is shown in the Fig. 9(e) and (f). Fig. 9(g) and (h) shows the misorientation angle distribution deformed at  $700\text{ }^\circ\text{C}$  and  $800\text{ }^\circ\text{C}$ , respectively. With the increasing of temperature, the percentage of high angle grain boundary increases. And it can be seen that the main distribution of the misorientation angle is concentrated at a small angle (LAGBs $<15^\circ$ ), which is related to the stored dislocations [120]. The fraction of LAGBs in Fig. 9(g) and (h) can indicate that the dislocation density deformed at  $700\text{ }^\circ\text{C}$  is higher than that of deformed at  $800\text{ }^\circ\text{C}$ . Moreover, it can also inferred that the recrystallized volume fraction increases due to the increasing temperature. The TEM micrographs of Cu-Fe-P alloy deformed at  $700\text{ }^\circ\text{C}$ ,  $0.01\text{ s}^{-1}$  is shown in Fig. 10. As illustrated in Fig. 10(a), it can be seen that the dislocations rearrange near the grain boundaries in order to reduce the stress concentration under the early stage of deformation, which is an early character of dynamic recrystallization [112,121]. With the development of deformation, a small angle grain boundaries were formed in the deformed grains due to the cross-slip or climb of dislocations. Finally, the small angle grain boundaries were transformed

into the recrystallized grains, which is characterized by almost no dislocation lines in the grains. In addition, there are some deformation bands and fine precipitated phase particles in the microstructure, which can hinder the migration of grain boundaries and movement of dislocations. The precipitates can be determined to be  $CuP_2$  [46].

In the process of hot working, the deformation temperature and strain rate have great influence on the properties of the material after deformation. In order to reduce the deformation and cracking of materials, reduce the waste of resources and obtain the best hot working performance, the hot working diagram is drawn based on the Dynamic Material Modeling (DMM), which can determine the hot working process parameters (including deformation temperature and strain rate) [122–124]. The best hot working area can be found directly from the hot working diagram, and the working area that should be avoided in the process of alloy hot deformation can also be determined. Wu et al. [125] obtained the parameters suitable for hot working based on the processing maps with  $1100\text{--}1200\text{ }^\circ\text{C}/0.01\text{--}0.5\text{ s}^{-1}$  and  $1100\text{--}1200\text{ }^\circ\text{C}/1.0\text{--}10\text{ s}^{-1}$ . Fig. 11 shows the hot processing maps of Cu-Fe-P, Cu-Fe-P-Ce and Cu-Fe-P-Y alloys. The grid area in the figure is unstable, while other areas are stable. Moreover, the number on the lines indicates the power dissipation value, and the size of the value indicates the amount of energy consumed by microstructure evolution. Therefore, the suitable hot working areas of the three alloys are  $620\text{--}850\text{ }^\circ\text{C}$ ,  $0.001\text{--}0.08\text{ s}^{-1}$ ;  $700\text{--}850\text{ }^\circ\text{C}$ ,  $0.001\text{--}0.14\text{ s}^{-1}$  and  $720\text{--}850\text{ }^\circ\text{C}$ ,  $0.001\text{--}0.16\text{ s}^{-1}$ , respectively.

Besides the thermal deformation behavior of copper alloys, it is also critical to investigate the aging behavior of copper alloy. Fig. 12 shows the TEM micrographs of Cu-Fe-P alloy aging at  $460\text{ }^\circ\text{C}$  for 20 min. It can be seen that there are some defor-





**Fig. 13 – The comprehensive properties of the Cu-Fe-P alloy with different types of alloy elements [25,117,119,126–136].**

mation bands, sub-grains and dislocated cells agglomerated together, which can hinder the migration of grain boundaries. In addition, there are fine precipitated phase particles with dispersion distribution and a small amount of growing precipitation phase, which can be determined to be  $\alpha$ -Fe [119]. In order to study the effect of adding elements on the conductivity and tensile strength of the Cu-Fe-P alloy, Fig. 13 show the relationship between electrical conductivity and ultimate tensile strength of the Cu-Fe-P alloys with different types of alloy elements. It can be seen that the addition of Cr and Sn makes the strength of the Cu-Fe-P alloy higher and the conductivity more decreased. Guo et al. [117] investigated the conductivity and mechanical properties of Cu-Fe-P alloy, the results show that the addition of Cr can significantly improve the physical properties and mechanical properties by promoting the dispersion of precipitated phase in matrix. Lu et al. [130] obtained a high electrical conductivity of Cu-Fe-P alloy by the B addition, which has a little negative effect on conductivity, but the tensile strength was relatively low. It is worth mentioning that the addition of Mg, Y and Ce elements has a good comprehensive performance for Cu-Fe-P alloy. Wang et al. [119] obtained a high conductivity and mechanical properties of Cu-Fe-P alloy by the addition of Y with a combined performance of 599 MPa and 71.1%IACS, which was attributed to the aging precipitation strengthening. In the end, other added elements have no significant effect on the Cu-Fe-P alloy for conductivity and mechanical properties.

## 5. Conclusions

In this review, the texture evolution and microstructure evolution under hot deformation of Cu-Ni-Si, Cu-Co-Si and Cu-Fe-P alloys were investigated. In order to analyze the texture evolution, the standard polar figures and ODF figures were established. The TEM analysis shows that the addition of trace elements promoted the dispersion of nanoscale precipitated phase particles in the matrix, which can hinder the movement of grain boundaries and dislocations during the hot deformation or aging processes. In addition, the suitable hot processing parameters of the Cu-Fe-P alloy were determined by the hot working diagram. Finally, the comprehensive diagrams for the influence of the alloying elements addition on the electrical

conductivity and ultimate tensile strength of the Cu-Ni-Si and Cu-Fe-P alloys were obtained.

## Conflicts of interest

The authors declare no conflicts of interest.

## Author Biography

Yongfeng Geng, Yijie Ban, Yi Zhang, Yanlin Jia, Baohong Tian, Yong Liu, Alex A. Volinsky, Kexing Song are mainly engaged in the research of thermal deformation and aging of advanced copper alloys; Bingjie, Wang is mainly engaged in the research of high entropy alloy; Xu Li is mainly engaged in the research of electron microscopy and stress measurement technology.

So far, three papers have been published in JAC and Vacuum as the first author (Yongfeng Geng, DOI: <https://doi.org/10.1016/j.jallcom.2019.153518>; <https://doi.org/10.1016/j.vacuum.2020.109376>; <https://doi.org/10.1016/j.jallcom.2020.155666>). In these three papers, the hot deformation behavior of Cu-Co-Si alloy and the effect of Ti and Ce addition on the hot deformation behavior of the alloy were investigated, mainly including the stress-strain curve, EBSD analysis and TEM characterization. The results show that the addition of alloying elements can inhibit the recrystallization of the alloy and improve the activation energy of hot deformation, which has a good effect.

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