High thermoelectric power factor in Cu-Ni alloy by potential barrier scattering of twin boundaries

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Abstract

Constantan alloy (Cu-Ni) has been known for a long time in thermocouples due to its thermal power property. In this study, we show an enhancement in thermoelectric performance of Cu₅₆Ni₄₂Mn₂ alloy by introducing nanoscale twins into its microstructure. Comparing to arc-melted ingot (without nanoscale twins), the ball milled and hot pressed (BM-HP) samples with twinning showed a higher Seebeck coefficient of $\sim -72.5 \mu\text{V K}^{-1}$ (an increase of $\sim 12\%$ at 873 K), a larger power factor of $\sim 102 \mu\text{W cm}^{-1} \text{K}^{-2}$ (an increase of $\sim 21\%$ at 873 K), and hence a higher ZT of ~ 0.19 (an increase of $\sim 34\%$ at 873 K). A high output power density of $\sim 53.4 \text{ W cm}^{-2}$ is calculated from the high power factor even though the conversion efficiency is lower than 3% due to the low ZT . TEM characterization shows there is a large quantity of nanoscale twins with spacing of 50 to 200 nm. It is very likely that low-energy carriers are selectively scattered by the twin boundaries (*i.e.*, potential barrier scattering) thus lead to enhanced Seebeck coefficient. The improved thermoelectric performance of nano-twinned Cu-Ni alloy suggests constantan could be promising in thermoelectric power

generation where the power output density is more important than the conversion efficiency.

Keywords: Thermoelectric; Cu-Ni alloy; Nanoscale twins; Potential barrier scattering;

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Introduction

Thermoelectric materials are a group of electronic materials that can convert thermal energy into electricity and vice versa.[1-3]The performance of thermoelectric materials is determined by figure of merit (ZT) that is defined as $ZT=S^2\rho^{-1}\kappa^{-1}T$, where S , ρ , κ , and T are Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively. Among them thermal conductivity contains the electronic thermal conductivity (κ_{ele}) and lattice thermal conductivity (κ_{lat}).

So far, the enhancement of ZT is mainly benefited from reduction of lattice thermal conductivity. By utilizing alloy scattering[4-7] and nanostructuring technique[8-14] lattice thermal conductivity can be decreased significantly. However, high ZT is not the only concern for thermoelectric power generation, a large output power is also needed.[15-18] Since the output power of thermoelectric module is directly related to the power factor of materials, therefore finding an effective way to improve power factor is very critical. Presently, there are several methods reported to be able to enhance thermoelectric power factor, including band engineering,[19, 20] resonant energy level,[21, 22] modulation doping,[23, 24] and potential barrier scattering.[25-27]

Since carriers with lower energy would contribute negatively to Seebeck coefficient, selective scattering of those low-energy carriers would effectively improve Seebeck coefficient and could lead to higher power factor (*i.e.*, potential barrier scattering).[28] Ravich has shown that the presence of potential barriers can result in a strong dependence of electron mean free path on energy near the chemical potential, if their height is close to Fermi level (η). Carriers of energy lower than barrier height are stopped, while most of those with energy above barrier pass through it.[25] The possible improvement of thermoelectric energy conversion efficiency by potential barrier scattering has been calculated by Nishio *et al.*,[29] which has already been validated experimentally.[26, 30-36] Kishimoto *et al.* investigated the potential barrier scattering by grain boundary for PbTe. Their results showed that the Seebeck coefficient increases monotonically with the decrease of grain size.[26] Heremans *et al.* reported the enhanced Seebeck coefficient in PbTe by potential barrier scattering from Pb nanoprecipitates.[36] It is noted that in order to realize potential barrier scattering, a suitable microstructure or nanostructure (*i.e.*, potential barrier) should be constructed. Presently, the microstructures that claimed to be able to realize potential barrier scattering are grain

boundary and nanoprecipitates. Generally, interfaces of these microstructures are highly distorted which would scatter a wide spectrum of carriers without the capability of preferably scattering low-energy carriers. So it is very difficult to realize the potential barrier scattering by using these microstructures. Thus, the question arises if there are any better microstructures that could more selectively scatter low-energy carriers.

Comparing to non-coherent grain boundaries and interfaces between nanoprecipitate and matrix, coherent twin boundaries will not strongly scatter carrier, which is favorable for thermoelectric materials to maintain a low electrical resistivity.[37] However, the twin boundaries should be able to scatter low-energy carriers, therefore it could enhance the Seebeck coefficient by potential barrier scattering. To our best knowledge, the effects of twin boundaries on thermoelectric properties of materials are scarcely investigated, and the possibility of potential barrier scattering by twin boundaries has never been studied.

Therefore, the motivation of this work is to investigate the possibility of potential barrier scattering by twin boundaries. So far, there are many research reported about the formation of twins. Lu *et al.* prepared high density of nanoscale twins in copper by using pulse electrodeposition.[37-39] According to their results, the nano-twinned copper showed comparable electrical conductivity to that of coarse-grained copper, which clearly shows the coherent characteristic of twin boundaries.[40] Moreover, Huang *et al.* reported the formation of twins in ball-milled copper powder.[41] In this work, Cu-Ni alloy (specifically, constantan alloy) is chosen, and there are three main reasons for this choice. Firstly, based upon previous research it is very likely that we could prepare Cu-Ni alloy with twins by ball milling method. Secondly, the constantan alloy has a higher Seebeck coefficient ($\sim 40 \mu\text{V K}^{-1}$ at room temperature) than other metallic materials, which contributed to its high power factor ($\sim 40 \mu\text{W cm}^{-1} \text{K}^{-2}$ at room temperature).[42-44] Thirdly, constantan alloy has a good high temperature thermal stability and oxidation resistance. If its thermoelectric performance can be improved it could be promising for thermoelectric power generation. In this work, ball milled and hot pressed (BM-HP) Cu-Ni alloys with nanoscale twins were prepared and showed higher Seebeck coefficient than that of arc-melted ingot. Selenium (Se) was found to help the ball milling process and the amount of Se and hot pressing temperature showed no obvious effect on Seebeck coefficient. Therefore, the enhanced

Seebeck coefficient for the BM-HP samples should most likely due to the existence of nanoscale twins. The twin boundaries could be able to selectively scatter low-energy carriers thus increased the Seebeck coefficient by potential barrier scattering.

Experiment

Synthesis

Copper powder (99.5%, Alfa Aesar), nickel powder (99.8%, Alfa Aesar), manganese pieces (99.8%, Alfa Aesar) were weighed according to the composition of $\text{Cu}_{56}\text{Ni}_{42}\text{Mn}_2$. Besides, in order to prevent materials become too sticky to the jar and balls during ball milling, some Se is added. The materials are loaded into stainless steel jar in glove box under argon atmosphere with oxygen level lower than 3.5 ppm. The materials were ball milled directly for 20 hours at 1200 rpm. The ball-milled powders were then loaded into a graphite die with an inner diameter of 12.7 mm in glove box. The graphite die with loaded powder was removed from glove box and immediately hot pressed by dc-HP at 1073 K for 2 min into a disk with thickness of 2-3 mm. For comparison, a sample with composition of Se free is also prepared by arc melting method.

Thermoelectric property characterization

All the samples were cut into about 2 mm × 2 mm × 12 mm for simultaneous electrical resistivity and Seebeck coefficient characterizations under Helium atmosphere (ZEM-3; ULVAC Riko). Thermal conductivity $\kappa = dDC_p$ was calculated using measured density (d) by Archimedeian method, specific heat (C_p) by differential scanning calorimetry (DSC 404C; Netzsch) and thermal diffusivity (D) by laser flash method (LAF457; Netzsch). All the thermoelectric parameters were measured from room temperature to 873 K. The errors of measurement for electrical resistivity, Seebeck coefficient, and thermal conductivity are $\pm 5\%$, $\pm 5\%$, and $\pm 7\%$, respectively. Hall coefficient R_H was measured at room temperature on a commercial system (PPMS; Quantum Design) using a four-probe configuration, with the magnetic field sweeping between ± 9 T and an electrical current between 10 and 20 mA. The Hall carrier concentration n_H is calculated from the relations $n_H = 1/(e R_H)$. Due to the high carrier concentration of constantan, high magnetic field is used during the Hall measurement.

Phase composition and nanostructure

The phase composition of samples was characterized by X-ray diffraction (PANalytical X'pert PRO diffractometer with a Cu K α radiation source). The lattice constants of BM-HP sample were calculated by Rietveld refinement using the Fullprof software. The crystal structure of Nickel (#103063, ICSD database) was chosen as the starting structure. Specimens for electron microscope investigations were prepared by a standard procedure, including grinding, mechanical polishing, dimpling and final ion-beam milling. The selected area electron diffraction (SAED) and high-resolution electron microscopy image (HREM) investigations were performed with a JEM-2010 electron microscope operated at the accelerating voltage of 200 kV.

Results and discussion

Phase composition and Rietveld refinement

Fig. 1 shows the XRD patterns of Cu-Ni alloys that can be indexed to the FCC crystal structure (PDF-#04-0836). The peaks of BM-HP sample and arc-melted ingot are between standard peaks of Cu and Ni (Fig. 1a). Moreover, arc-melted ingot showed preferred orientation, which was very likely caused by the forced cooling of water cooled hearth. Since constantan alloy has FCC structure that is isotropic, therefore the preferred orientation of ingot should not influence its thermoelectric properties. The enlarged view of Fig. 1a is shown in Fig. 1b. Comparing to arc-melted ingot, BM-HP sample showed four peaks between the angle of 30° to 42°. The peak around 32.5° can be indexed to MnSe while there are three other peaks which cannot be identified so far. It is noted that the intensity of these minor peaks are higher for higher Se content sample than that of lower Se content sample (Supplementary information, Fig. S1). Moreover, since Se has a very low solubility in Cu (< 0.002 wt.%, at room temperature), it is reasonable to infer that these peaks should belong to Se-related phases.[45]

In order to further verify the formation of solid solution, the lattice constants are calculated by Rietveld refinement. Fig. 2 shows the Rietveld refinement of BM-HP sample. The lattice constants for pure Copper and Nickel are 3.615 Å and 3.524 Å, respectively. The calculated lattice

constant for the BM-HP Cu-Ni alloy is 3.574 Å, which shows a good agreement with the Vegard's law. It indicates the successful formation of solid solution for the BM-HP Cu-Ni alloys.

Nanoscale twins

In order to investigate the nanostructures of arc-melted ingot and BM-HP sample, HRTEM characterizations are carried out. Fig. 3a shows the TEM image of arc-melted ingot. There is no special microstructures observed in this specimen. However, for BM-HP sample, it is clear that there are many nanoscale twins in the crystalline grains with spacing about 50 to 200 nm (Fig. 3b). It is noted that the distribution of nanoscale twins varies from region to region (Supplementary information, Fig. S2).

Fig. 4a shows the TEM image of nanoscale twins in BM-HP sample. Fig. 4b is a SAED pattern for one of the twins in BM-HP samples, which can be indexed as [101] according to $Fm\bar{3}m$ cubic structure. It is a superposition of two sets of the diffraction spots with [111] direction as twinning axis. The schematic view of Fig. 4b is shown in Fig. 4c with the red filled circles and blue unfilled circles representing the diffraction spots from neighboring grains. The rotation angle between these two grains is 120°. HRTEM image corresponding to Fig. 4b is shown in Fig. 4d where the twin boundary is situated in (111) plane marked by the white arrows. The measured angle between the crystal lattice on both sides of the boundary is about 120° as mentioned above. Comparing to the nanoscale twins reported by Lu *et al.*, [37] the twins formed in our work showed larger dimension. It could be explained by different preparation methods used in our work.

To understand the twinning in Cu-Ni alloys, the nanostructure of ball-milled powder is also characterized by HRTEM. As shown in Fig. 5a, nanoscale twins with spacing of 5 to 8 nm exist in the ball-milled powders. The SEAD pattern in the inset can be successfully indexed by the crystal structure of Cu-Ni alloys, which shows a good agreement with the XRD results and Rietveld refinement. The magnified image of twin boundaries is shown in Fig. 5b, which is marked by the white arrows. Similar to the results reported by Huang *et al.*, [41] the twins of Cu-Ni alloys are indeed formed during the ball milling process. The reason for twinning can be explained as: the shear stress induced by ball milling exceeds the critical shear stress for twinning; the grain size decreases to

critical value below which twinning rather than slip is the preferred mode of deformation as well as the high strain rate of ball milling.[41] It is noted that comparing to the twins in the BM-HP samples (Fig. 3b or Fig. 4a), the twins in the ball-milled powders have much smaller spacing. It is reasonable to infer that during the hot pressing process the nanoscale twins in the ball-milled powder went through a significant twin growth.

Thermoelectric properties

Fig.6 shows the temperature dependent thermoelectric properties of arc-melted ingot and nano-twinne samples. Comparing to arc-melted ingot, nano-twinne samples show higher electrical resistivity (Fig.6a). The room temperature electrical resistivity for nano-twinne sample is $\sim 5.2 \times 10^{-7} \Omega \text{ m}$ and is $\sim 4.8 \times 10^{-7} \Omega \text{ m}$ for arc-melted ingot. The higher resistivity of nano-twinne samples could be explained by scattering of electrons by secondary phases, and twin boundaries (details will be discussed later). As shown in Fig. 6b, both nano-twinne samples and arc-melted ingot showed negative Seebeck coefficients that indicate n-type conduction. Moreover, the nano-twinne sample showed a higher Seebeck coefficient than that of arc-melted ingot in the whole temperature range. For arc-melted ingot, its room temperature Seebeck coefficient is $\sim -42.4 \mu\text{V K}^{-1}$ and increases to $\sim -65.7 \mu\text{V K}^{-1}$ at 873 K. The room temperature Seebeck coefficient of nano-twinne sample is $\sim -45.7 \mu\text{V K}^{-1}$ and it reaches $\sim -72.5 \mu\text{V K}^{-1}$ at 873 K. Comparing to arc-melted ingot, the nano-twinne sample showed a $\sim 12\%$ enhancement of Seebeck coefficient at 873 K. The details for the improved Seebeck coefficient will be discussed later. Moreover, It is noted that the arc-melted ingot showed almost identical Seebeck coefficient to that of standard constantan sample (which is used for ZEM machine calibration). The increased Seebeck coefficient leads to improved power factor (Fig. 6c). At 873 K, the PF of arc-melted ingot is $\sim 84.6 \mu\text{W cm}^{-1} \text{ K}^{-2}$ and it increases to $\sim 102 \mu\text{W cm}^{-1} \text{ K}^{-2}$ for nano-twinne samples, an enhancement of $\sim 21\%$. Comparing to other high PF thermoelectric materials, *i.e.*, Skutterudite, Half-Heusler, and $\text{Mg}_2\text{Sn}_{0.75}\text{Ge}_{0.25}$, the Peak PF is $55 \mu\text{W cm}^{-1} \text{ K}^{-2}$ at 850 K for $\text{Ba}_{0.1}\text{La}_{0.05}\text{Yb}_{0.07}\text{Co}_4\text{Sb}_{12}$, [46] $52 \mu\text{W cm}^{-1} \text{ K}^{-2}$ at 723 K for $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{NiSn}$, [47] and $55 \mu\text{W cm}^{-1} \text{ K}^{-2}$ at 623 K for $\text{Mg}_2\text{Sn}_{0.75}\text{Ge}_{0.25}$, [16] the nano-twinne Cu-Ni alloy showed almost doubled PF . To our best knowledge, this is the highest PF ever been reported at similar temperature.

It is also noted that arc-melted ingot shows comparable PF to that of standard constantan sample.

As shown in Fig. 6d and inset, the thermal diffusivity of arc-melted ingot is slightly higher than that of nano-twinned sample. Therefore, the arc-melted ingot showed higher thermal conductivity than that of nano-twinned sample in the whole temperature range (Fig. 6e). At 873 K, the thermal conductivity of nano-twinned sample is $\sim 47.9 \text{ W m}^{-1} \text{ K}^{-1}$ and it is $\sim 53.4 \text{ W m}^{-1} \text{ K}^{-1}$ for arc-melted ingot. The higher thermal conductivity of the ingot is mainly due to its lower electrical resistivity. Since Cu-Ni alloy is metal, its thermal conductivity is dominated by the electronic thermal conductivity while the lattice thermal conductivity is negligible which is totally different from the semiconductor materials. According to the Wiedemann–Franz relation, the electronic thermal conductivity is $\kappa_{ele} = LT/\rho$, where L is Lorenz number, $2.44 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$. Combined with increased PF and decreased thermal conductivity, ZT of nano-twinned samples is slightly improved (Fig. 6f). The peak ZT (at 873 K) of arc-melted ingot is ~ 0.14 and it increases to ~ 0.19 for nano-twinned sample, an enhancement of $\sim 36\%$. Moreover, it is worth pointing out that all the samples showed repeatable properties upon thermal cycling, which indicates good thermal stability.

Calculation of output power density and efficiency

The conventional ZT and PF have been used for more than half a century to guide the research of thermoelectric materials. Recently, Kim *et al.* showed that the conventional ZT often lead to large errors in calculation of leg efficiency and output power using the conventional energy conversion efficiency and output power formulas.[17, 48] Therefore, they introduced the following new formulas to accurately calculate the energy conversion efficiency and output power by defining a new engineering power factor $(PF)_{eng}$ and figure of merit $(ZT)_{eng}$ and taking into account of temperature dependent individual thermoelectric properties and Thomson effect.

$$\omega_{\max} = \frac{1}{4} \frac{(T_H - T_C)^2}{L_{leg}} (PF)_{eng} \quad (1)$$

$$\eta_{\max} = \eta_c \frac{\sqrt{1 + (ZT)_{eng} (\alpha_1/\eta_c)} - 1}{\alpha_0 \sqrt{1 + (ZT)_{eng} (\alpha_1/\eta_c)} + \alpha_2} \quad (2)$$

where

$$(PF)_{eng} = \frac{\left(\int_{T_C}^{T_H} S(T)dT\right)^2}{\int_{T_C}^{T_H} \rho(T)dT} \quad (3)$$

$$\eta_C = \frac{T_H - T_C}{T_H} \quad (4)$$

$$(ZT)_{eng} = \frac{(PF)_{eng}}{\int_{T_C}^{T_H} \kappa(T)dT} (T_H - T_C) \quad (5)$$

$$\alpha_i = \frac{S_{T_H} (T_H - T_C)}{\int_{T_C}^{T_H} S(T)dT} - \frac{\int_{T_C}^{T_H} \tau(T)dT}{\int_{T_C}^{T_H} S(T)dT} W_T \eta_C - i W_J \eta_C \quad (i = 0, 1, 2) \quad (6)$$

$$\tau = T \frac{dS}{dT} \quad (7)$$

$$W_T = \frac{\int_{T_C}^{T_H} \int_{T_C}^{T_H} \tau(T)dTdT}{\Delta T \int_{T_C}^{T_H} \tau(T)dT} \quad (8)$$

$$W_J = \frac{\int_{T_C}^{T_H} \int_{T_C}^{T_H} \rho(T)dTdT}{\Delta T \int_{T_C}^{T_H} \rho(T)dT} \quad (9)$$

in which ω_{max} is the maximum output power density, T_H is the hot side temperature, T_C is the cold side temperature, L_{leg} is the length of leg, η_{max} is the maximum energy conversion efficiency, η_C is the Carnot efficiency, S_{T_H} is the Seebeck coefficient at hot side, τ is the Thomson coefficient, W_T is the weight factor of Thomson heat, and W_J is the weight factor of Joule heat.

The boundary conditions are $T_C = 373$ K, $L_{leg} = 2$ mm, T_H is from 373 K to 873 K. The engineering $(PF)_{eng}$ and $(ZT)_{eng}$ as a function of T_H are shown in Fig. 7a and Fig. 7b. The nano-twinned samples showed a higher $(PF)_{eng}$ than that of arc-melted ingot. At $T_H = 873$ K, the $(PF)_{eng}$ is ~ 4.3 W $m^{-1}K^{-1}$ for nano-twinned samples and ~ 3.5 W $m^{-1}K^{-1}$ for arc-melted ingot. The nano-twinned samples also showed a higher $(ZT)_{eng}$ than that of arc-melted counterpart. At $T_H = 873$ K, the $(ZT)_{eng}$ is ~ 0.09

for the ingot and is ~ 0.12 for nano-twinned samples. Due to the relationship between $(PF)_{eng}$ and output power density shown in eq (1), the nano-twinned samples also showed a higher output power density than arc-melted ingot (Fig 7c). The output power density is $\sim 43.6 \text{ W cm}^{-2}$ for arc-melted ingot and it reaches to $\sim 53.4 \text{ W cm}^{-2}$ for nano-twinned samples, an enhancement of $\sim 23\%$. Moreover, output power are also calculated for other thermoelectric materials (Supplementary information S3). Due to the high power factor of nano twinned Cu-Ni alloy, it showed much higher output power than that of other materials. It should be pointed out that even though Cu-Ni alloy does show very high output power density, it does not mean it is practically possible to achieve such high power density unless the heat transfer has no limit. The efficiency for arc-melted ingot is 2.0% and it increases to 2.7% for nano-twinned samples, an increase of 35%. It is noted that although the energy conversion efficiency of Cu-Ni alloys are still low at present (Fig. 7d), their excellent output power density enables this material to be possibly used in power generation when capacity of the heat source is huge (*i.e.*, solar heat) or the cost of heat source is not a big factor.[16]

Potential barrier scattering by twin boundary

The enhancement of Seebeck coefficient for nano-twinned samples is quite interesting and it is the key factor for the improved thermoelectric performance here. In order to investigate the origin of the improved Seebeck coefficient, the effects of Se content and hot pressing temperature are investigated.

As shown in Fig. 8a, BM-HP samples with different Se content ($\text{Cu}_{56}\text{Ni}_{42}\text{Mn}_2\text{Se}_x$, $x = 1, 2, 3, 4$) showed almost identical Seebeck coefficient in the whole temperature range. For BM-HP samples ($\text{Cu}_{56}\text{Ni}_{42}\text{Mn}_2\text{Se}_1$) prepared at different hot pressing temperatures they showed similar Seebeck coefficient values within the measurement error (Fig. 8b). Although, none of these factors showed obvious influence on the enhancement of Seebeck coefficient, it is noted that all the nano-twinned BM-HP samples showed higher Seebeck coefficient than that of arc-melted ingot. Therefore, the existence of nanoscale twins in BM-HP samples could be the most likely reason for the enhanced Seebeck coefficient. Thus, the possibility of Seebeck coefficient enhancement by twin boundaries is discussed here.

As shown in Fig. 9, many nanoscale twins exist in the grains of BM-HP Cu-Ni alloys. Due to

the coherent characteristic of twin boundaries, most of the high-energy carriers will be unaffected by twin boundaries, which enables the nano-twinned samples maintain a good electrical conductivity. However, for low-energy carriers, lower than the height of potential barrier, they could be effectively scattered. The selective scattering of low-energy electrons will lead to enhanced Seebeck coefficient (*i.e.*, potential barrier scattering). It is noted that the height of the potential barrier plays a decisive role in the scattering mechanism. In order to effectively filter out the low-energy carriers the height of potential barrier should not be too high. The non-coherent interfaces (grain boundaries and interfaces between nanoprecipitate and matrix) could severely distort the lattice periodic potential that lead to an unfavorably high potential barrier. On the contrary, due to the coherent characteristic of twin boundaries, the potential barrier by twin boundaries should be much lower and could selectively scatter low-energy carriers while high-energy carriers are unaffected. Thus, it explained the reason why twin boundaries would be more effective in the potential barrier scattering than that of grain boundaries and nanoprecipitates.

Pisarenko line

In order to further investigate the electrical properties of the Cu-Ni alloys, the Hall measurement is carried out. Using the measured Hall carrier concentration and Seebeck coefficient, the Pisarenko relationship between Seebeck coefficient and carrier concentration is plotted. The well-established Pisarenko line illustrates the dependence of Seebeck coefficient on carrier concentration for semiconductor materials.[4, 21] Although the constantan alloy is metal and the Pisarenko line is not directly suitable, we can still be inspired from it.

As shown in Fig. 10, the arc-melted ingot showed a good agreement with the Pisarenko line with the Density-of-states (DOS) effective mass of $\sim 7.5m_0$ (m_0 is free electron mass). It is clear that all the nano-twinned samples are above this line. For metals, the Seebeck coefficient can be expressed by the following equation:[7]

$$S = \mp \frac{\pi^2}{3} \frac{k}{e} \frac{(r+3/2)}{\eta} \quad (10)$$

where k is the Boltzmann constant, e is the electron charge, and r is the scattering factor for carriers.

Since the nano-twinned samples have higher Hall carrier concentration than that of arc-melted ingot, it means that their Fermi level η are higher than that of the arc-melted ingot. So the improved Seebeck coefficient of nano-twinned samples can only be explained by the increased scattering factor r . The increased r is an indication for the enhanced scattering of carriers in the nano-twinned samples, which could be explained by the scattering of low-energy carriers by twin boundaries. Therefore, it further explained that the higher Seebeck in nano-twinned samples is due to the potential barrier scattering of the twin boundaries. It should be pointed out that the higher carrier concentration of the hot pressed sample than that of the arc-melted ingot could be explained by the higher density of defects in the ball milled and hot pressed sample. As has already been pointed out by several researchers, some structural defects can serve as an important doping mechanism.[9, 49] During the high energy ball milling process many defects are formed in the ball-milled Cu-Ni nanopowders (Supplementary information, Fig. S4). These defects could lead to a higher carrier concentration for the hot pressed Cu-Ni sample.

Conclusion

In summary, the nano-twinned Cu-Ni samples and arc-melted Cu-Ni ingot are prepared and characterized. The results show that comparing to arc-melted ingot, nano-twinned samples showed higher Seebeck coefficient (an increase of $\sim 12\%$ at 873 K) and larger power factor (an increase of $\sim 21\%$ at 873 K), hence a higher ZT of ~ 0.19 (an increase of $\sim 34\%$ at 873 K) can be achieved. Moreover, a high output power density of $\sim 53.3 \text{ W cm}^{-2}$ (at $T_H = 873 \text{ K}$) can be obtained by nano-twinned samples. The enhanced thermoelectric properties of nano-twinned samples could be explained by the potential barrier scattering of the twin boundaries.

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Figures

Figure 1. (a) XRD patterns of BM-HP samples and arc-melted ingot, (b) enlarged view from (a).

Figure 2. Rietveld refinement of BM-HP Cu-Ni alloy.

Figure 3. TEM results of arc-melted ingot and BM-HP samples. (a) Image for arc-melted ingot, (b) image showing the nanoscale twins in BM-HP samples.

Figure 4. TEM results of BM-HP samples. (a) Image of the nanoscale twins in BM-HP sample, (b) [101] zone-axis SAED pattern taken from the twin boundary, (c) schematic drawings of the diffraction spots for (b) and (d) HRTEM image corresponding to (b) with the arrows pointing out the twin boundary.

Figure. 5 HRTEM results of ball-milled powders. (a) Image of nanoscale twins in the ball-milled powders, inset shows the SEAD pattern, (b) Magnified image for the twin boundaries.

Figure 6. Comparison of thermoelectric properties of arc-melted ingot and nano-twinned sample. (a) Electrical resistivity ρ , (b) Seebeck coefficient S , (c) power factor PF , (d) thermal diffusivity D , (e) total thermal conductivity κ_{total} , (f) figure of merit ZT .

Figure 7. (a) Dependence of $(PF)_{eng}$ on hot side temperature T_H , (b) dependence of $(ZT)_{eng}$ on hot side temperature T_H , (c) dependence of output power density ω_{max} on hot side temperature T_H , (d) dependence of efficiency η_{max} on hot side temperature T_H .

Figure 8. (a) Effect of Se content ($\text{Cu}_{56}\text{Ni}_{42}\text{Mn}_2\text{Se}_x$, $x = 1, 2, 3, 4$) on the Seebeck coefficient of Cu-Ni alloys, and (b) effect of hot pressing temperature (for $\text{Cu}_{56}\text{Ni}_{42}\text{Mn}_2\text{Se}_1$) on the Seebeck coefficient of Cu-Ni alloys.

Figure 9. Schematic view of potential barrier scattering by twin boundaries.

Figure 10. Dependence of Seebeck coefficient on Hall carrier concentration, *i.e.*, Pisarenko line.