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Mechanical property improvement induced by nanoscaled deformation twins in cold-sprayed Cu coatings

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ABSTRACT

Nanoscaled deformation twins have been observed in cold sprayed Cu coatings and the coating hardness has been improved by this kind of tiny twins. Strain rate up to 10^9 s^{-1} at the impact interfaces can be achieved at the cold spray process, and the maximum shearing compressive stress and tensile stress are 392 MPa and 397 MPa, respectively, obtained from impacting simulations. They are larger than the required shearing stress for the formation of deformation twins in Cu. The orientation relationship between the stripes can be determined to be $(11\bar{1})_M||(11\bar{1})_T$ and $(\bar{1}10)_M||(101)_T$ both in coatings prepared by cold spray Cu particles annealed at 700 °C and 250 °C, respectively. The hardness of the coatings is higher than that of the corresponding substrates which indicates the improvement by the work hardening effect in the cold spray process. Though the misorientation of the deformation twins in the coatings slightly deviates from 60°, the existence of nanoscaled deformation twins improves its hardness significantly.

1. Introduction

Nanoscaled twins have been widely investigated due to their specific effect on simultaneously improving strength and ductility. Studies showed that the strength, ductility and work hardening of nanotwinned Cu (nt-Cu) are influenced by the twin lamellar thickness (λ). For example, the yield strength of such nt-Cu first increases as twin thickness decreases [1,2], reaching a maximal strength of 900 MPa at $\lambda \approx 15$ nm. Interestingly, a pronounced increment in tensile uniform ductility and work hardening is observed in nt-Cu with monotonically decreasing λ [3]. Up to now, severe plastic deformation and pulse electrolytic deposition are the most effective methods to obtain nanoscaled twins or lamellas in Cu.

It is worth noting that, cold spray is a kind of low-temperature solid-state coating process in which spray particles undergo extensive plastic deformation at extremely high strain-rates (up to 10^9 s^{-1} at impact interfaces) [4]. Coatings of soft metallic materials, such as copper, aluminum, titanium and metal matrix composites can be easily formed using the cold spray technique [5–10]. Cold sprayed coatings have been well studied due to the advantages in mechanical properties, corrosion resistance, electronic as well as thermal conductive properties [11,12]. The increase in strength and hardness is attributed to the work hardening effect or grain refinement which is introduced in the cold spray process [13–15]. It is well known that deformation temperature, strain rate, grain size as well as alloying elements are the factors that influence the work hardening effect. Generally, the increase of dislocation density and the tangling of the dislocations cause the work hardening in cold spray. However, there are evidences that the deformation twins improve the mechanical property not only in hcp metals [16–18] in which the slip systems are limited, but also in fcc polycrystals in which the slip systems are more and dislocation motion can easily occur [19–21]. In cold sprayed Cu coatings, the exterior of the deposited Cu particles experiences extensive deformation, while the slight deformation in the interior of particles, which is due to the localized deformation and adiabatic shear instability occurring in the cold spray process. Therefore, the strain rate at the edge of each particle is larger than that in the center of it. As a result, there would be deformation twins in large deformed zone and sometimes dynamic recrystallization in small deformed zone. Therefore, the appearance of deformation twins in the cold sprayed Cu coatings may lead to the increase of hardness especially when the twins are in nanoscale. In this paper, the microstructure of cold sprayed Cu coatings was observed as well as the nanoidentation was performed in order to evaluate the coating mechanical properties, and the effect of nanoscaled deformation twins on the improvement of hardness was discussed.

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2. Material and methods

A spherical gas-atomized Cu powder (−120 + 150 mesh, LERMPS Lab, France) was selected as the original material. To investigate the influence of grain size on the microstructure and mechanical property of the coating, two kinds of heat treatments were performed on the original powder. One is annealed at 700 °C for 24 h in vacuum in order to relieve the residual stresses and get as larger as possible grain size. The other one is annealed at 250 °C for 24 h in vacuum in order to relieve the residual stresses. These two kinds of powders are deposited onto the Cu substrate by cold spraying. The used spray nozzle had an expansion ratio of about 4.9 and a divergent section length of 170 mm. High compressed air was used as the accelerating gas at a pressure of 2.8 MPa and temperature of about 550 °C, while argon was used as powder carrier gas at a pressure of 3.0 MPa and flow rate of 40 L/min. The standoff distance from the nozzle to the substrate surface was 30 mm. The transverse speed of spray gun was 100 mm/s for coating deposition. Finally, coatings about 200 µm were fabricated by cold spraying method described above with powders annealed at 700 °C and 250 °C for 24 h, respectively.

Microstructures of the powder and coatings were examined with an Optical Microscope (OM) (OLYMPUS GX71, Japan). Orientations of twins were investigated by Electron Backscattered Diffraction (EBSD) and Transmission Electronic Microscopy (TEM) techniques. EBSD samples were polished by both mechanical and vibrating methods and carried out at room temperature by using the Scanning Electron Microscopy (SEM, TESCAN MIRA3 XMU) equipped with an EBSD detector (Oxford Nordlys). The scanning step size was chosen to be 0.6 µm and 0.05 µm for substrates and coatings, respectively. TEM observation and Selected Area Electron Diffraction were conducted on FEI Tecnai F30 equipment. Microhardness of both coatings and substrates were tested in-situ by a Hysitron PI 87 indenter equipped on FEI Helios 600 SEM, in which the loading was constant for each point (2000 µN) and the displacement was measured for comparing the hardness.

3. Results and discussion

Fig. 1 shows the cross-sectional microstructure of original particles and particles annealed at 700 °C and 250 °C for 24 h. It is obvious that annealing at 700 °C and 250 °C for 24 h results in the difference in grain size of the Cu particles. The grains of the particle annealed at 700 °C for 24 h penetrate across it since they grow as large as possible, while the grains in the particle annealed at 250 °C for 24 h are still with the same size as the original ones. Nevertheless residual stresses could be released due to both kinds of annealing. It can be seen that the grain boundaries of Sample-700 are not so clear comparing with that of Sample-250 due to the obvious growing up of grains at the annealing process, as described in our previous work [22]. Besides the difference in grain size, there are some stripe-like microstructures in the interiors of grains. The stripes exist both in Sample-700 and Sample-250, which are proved to be deformation twins by using EBSD and TEM as follows.

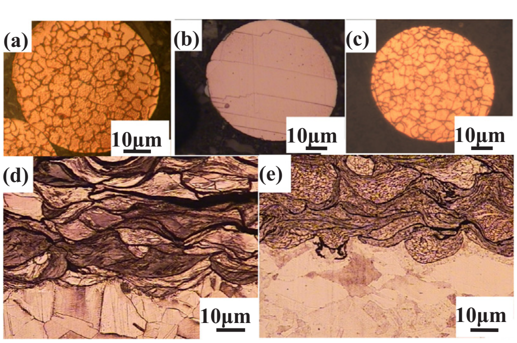

Fig. 1. Cross-sectional microstructure of original Cu particles (a) and particles annealed at 700 °C (b) and 250 °C (c) for 24 h, as well as the micrographs of the coatings deposited with the particles annealed at 700 °C (d) and 250 °C (e).

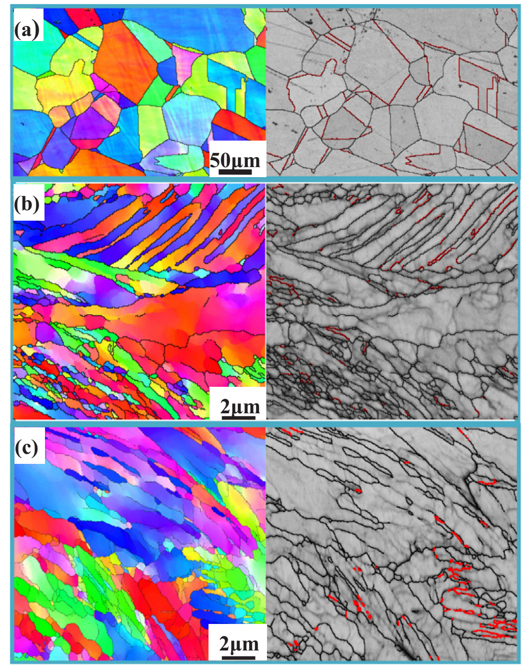

Fig. 2. Inverse Pole Figure (IPF) images and the corresponding grayscale images with large-angle grain boundaries (red lines are identified as the boundaries of misorientation angle equals to 60 ± 5°) of the substrate (a) and the coatings in Sample-700 (b) and Sample-250(c).

EBSD orientation contrast and the corresponding grain boundaries of substrates and coatings are shown in Fig. 2. As similar to most of the annealed Cu, the grains of substrates are equiaxed. In order to identify the characteristics of the grain boundaries, we used grayscale image to show the grain boundaries including the high-angle grain boundaries as well as the twin boundaries for the substrates. The red lines in the grayscale images indicate the boundaries of misorientation angle of 60°, which are considered to be twin boundaries. It is observed that the twin boundaries of the substrates are straight, and distributed not only in the large grains, but also interior of some small grains as shown in Fig. 2(a). In addition, the twins observed in the Cu substrates are represented as 60° < 111 >, that is a 60° rotation about < 111 > axes with the {111} twinning plane. The EBSD orientation contrast and corresponding grain boundaries of the cold-sprayed coatings in Sample-700 and Sample-250 are demonstrated in Fig. 2(b) and (c). It is interesting that the stripes of coatings observed in Fig. 1 are also seen in the orientation contrast images, and the orientations of these stripes can be observed from the difference in color. After analyzing, the boundaries of misorientation angle of 60° are indicated with red lines in the corresponding grayscale images. These red lines are not so straight and uncontinuous comparing with those twin boundaries in substrates. As being analyzed by Channel 5 software, it is revealed that the misorientation angle of the uncontinuous part of boundaries is slightly deviated from 60° due to the orientation variation in a stripe.

Stripes in the cold-sprayed coatings can also be evaluated by TEM, and misorientation between these stripes can be confirmed by the Selected Area Electronic Diffraction (SAED). Fig. 3(a) and (b) are the bright field images of the stripes in Sample-700 and Sample-250, respectively. It is clearly observed that the stripes are inhomogeneous in thickness with dimension of several nanometers to hundreds of nanometers. Interfaces of the stripes are relatively straight as shown in the images due to the comparatively local area, thus the stripes appear as plate-like in TEM images.

Corresponding SAED around the interface of stripes is inserted in

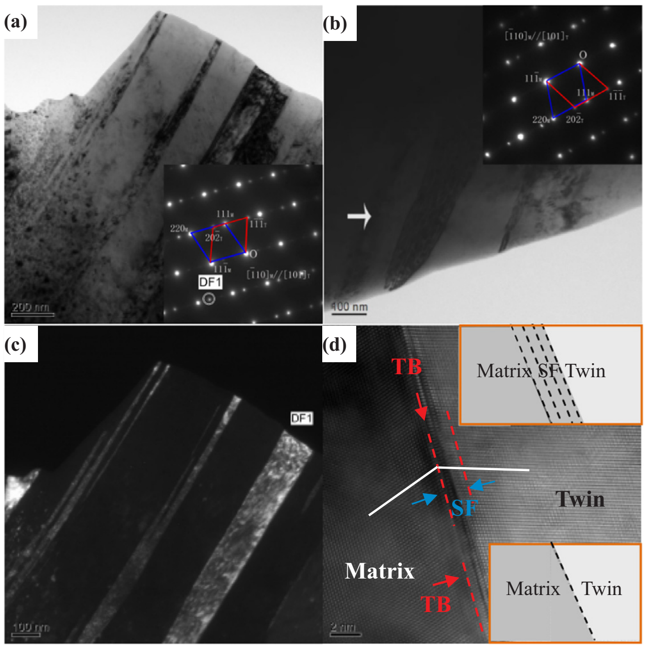

Fig. 3. TEM images of stripes in Sample-700 and Sample-250. (a) bright field image of Sample-700; (b) bright field image of Sample-250; (c) dark field image of figure (a); (d) HRTEM image and sketch map of twin boundary in Sample-700.

the images. It is interesting that the SAED patterns are obviously twin diffraction. The twin boundary is confirmed to be $(11\bar{1})$ plane, and the orientation relationship between the plates can be determined to be $(11\bar{1})_M||(11\bar{1})_T$ and $(\bar{1}10)_M||(101)_T$ both in Sample-700 and Sample-250. Fig. 3(c) shows the dark field image taken from the same area with Fig. 3(a), it shows that the stripes in the coating more clearly. High Resolution Transmission Electron Microscopy (HRTEM) image around the twin boundary (TB) indicates the TB without Stacked Faults (SF) along it can be considered as coherent boundary, while the TB with SF besides it is incoherent twin boundary. The alternation of these two kinds of boundaries leads to the variation of twin variant width, whereas the relationship between twin variants is not changed by the SF.

Load/unload experiments are obtained by nanoidentation accessory attached to SEM. Therefore, the nanoidentation experiments were operated so carefully that the indentation was located just at the interior of the particles which are the small deformed areas. Indent depth of the nanoindentation is about 500 nm which is much less than the thickness of the coatings thus the effect of substrate can be excluded. Elastic modulus and hardness of both substrate and coatings of Sample-700 and Sample-250 are calculated as shown in Table1. It can be seen that both elastic modulus and hardness of the coating are higher than those of the substrate, no matter the particles are annealed in 700 °C or 250 °C. The increase of elastic modulus and hardness can be attributed to the change in microstructure, that is, the appearance of deformation twins leads to the toughness of the coating. As we know, the deformation twins can be introduced during the extensively plastic deformation process with a large strain rate such as in blastic

Table1
Average elastic modulus and hardness of substrate and the coatings of Sample-700 and Sample-250.

	E(GPa)	H(GPa)
Substrate	77.29 ± 0.05	1.94 ± 0.05
Sample-700	102.14 ± 0.05	2.60 ± 0.05
Sample-250	82.85 ± 0.05	2.42 ± 0.05

deformation. This kind of deformation twins is the reason of work hardening during the rapid deformation process. Furthermore, it has been reported that nanoscaled growth twins prepared by means of severe plastic deformation and pulse electrolytic deposition have great effect on the strengthening and hardening of materials. In fact, it also can be proved via these experiments that hardness of coatings prepared by cold spray could be elevated to some extent due to the formation of nanoscaled deformation twins. Moreover, the elastic modulus and hardness of coating and substrate in Sample-700 are much higher than those in Sample-250. This can be explained that the residual stresses of the Cu particles annealed at 700 °C have been released more completely and thus the annealed Cu particles could absorb the deformation energy produced by the indenter and store the deformation energy after the work-hardening effect, which could resist the indenter force and provide lager elastic modulus.

Traditional methods for modifying the properties of metals are to alloy them with other elements to change their microstructure or their phase constitution. Introduction of structural defects provides another approach to modify the metal property, such as the well-known process of work-hardening. Besides the various possible point and line defects, interfaces are the most studied candidates which have great effect on improving mechanical property of materials. The strength of metals with nanoscaled grains can be an order of magnitude higher than that of their coarse-grained ones, owing to the high density of grain boundaries. Similarly, twin boundaries can thus act as stable interfaces for strengthening metals. In randomly oriented nanotwinned Cu, the tensile yield strength increases with the decrease of twin thickness (λ) and reaches a maximum for $\lambda = 15$ nm, which is similar with the dependence relationship on grain size of nanograin Cu. Besides thickness, the morphology of twins also influences the strength of metals. In parallel nanotwinned columnar Cu, the tensile yield strength increases with decreasing the twin thickness (λ) without any maximum value reported yet. In our experiment, the thickness of nanotwins in cold sprayed Cu coating varies from 10 nm to 200 nm, which is not so homogeneous as that of growth nt-Cu obtained in pulse electro-deposition Cu [2]. Deformation twinning as a common deformation mechanism has been described widely, and the formation of it needs to satisfy some conditions such as the strain rate and grain size.

Meyers has reported that plastic deformation by slip and twinning are considered as competitive mechanisms [23]. Strain rate, temperature, grain size are the factors which influence the slip twinning transition. As demonstrated in that paper, if there is plastic deformation in copper at ambient temperature, the twinning occurs at all strain rates for the grain size of 10 µm while plastic strain is 0.8 whereas no twinning is obtained at plastic strain of 0.2. Furthermore, the strain rate needed for the slip twinning transition decreases with increasing grain size. The strain rate of 10^6 s^{-1} is needed for twinning while grain size is 100 µm at ambient temperature. When grain size decreases to 20 µm, strain rate of 10^6 s^{-1} is just sufficient for twining at a lower temperature about 60 K. Actually, the average grain sizes of Sample-700 and Sample-250 are 50 µm and 10 µm, respectively, and the strain rate could achieve as high as 10^9 s^{-1} in our cold spray process. Therefore, deformation twinning occurs in both these two cold-sprayed coatings, which is in accordance with that calculated by Meyers [23].

Critical stress for the formation of deformation twinning can be calculated by simulation (ABAQUS Version 6.14) with considering the specific experiment condition on preparing coatings, such as particle sizes and speed of the particles [24,25]. The detailed simulation procedure could be found in the previous studies [26]. The shearing stress generated in the impact process between a Cu particle and substrate is shown in Fig. 4. It can be seen from the curves that the maximum shearing compressive and tensile stress during the impacting process both fluctuate at the range of 200–400 MPa. The maximum compressive stress and tensile stress are approximately 392 MPa and 397 MPa, respectively. At ambient temperature, the stress of about 300 MPa is required to produce the twinning when the strain rate is 0.8 and grain size

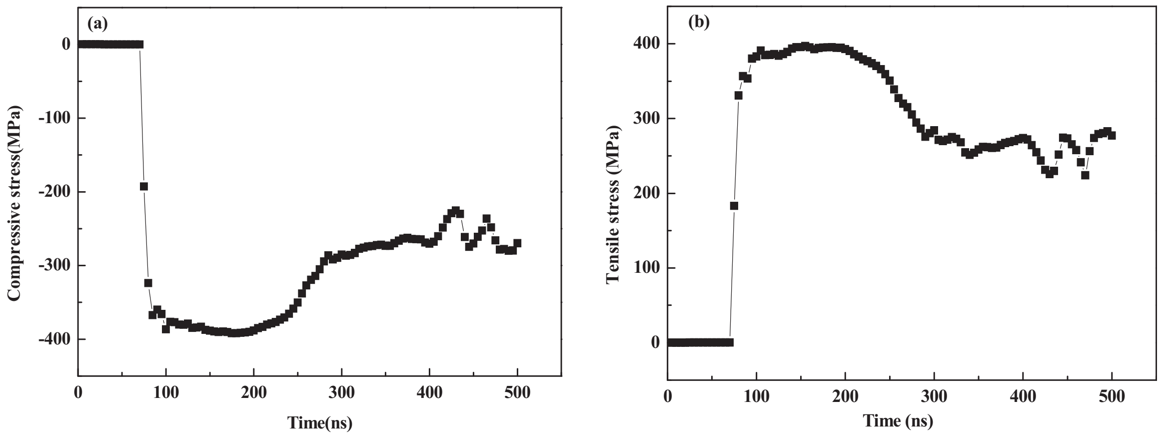

Fig. 4. Shearing stress between Cu particles and substrate in impacting process in sample-700 (a) compressive stress (b) tensile stress.

is 10 µm as demonstrated in the literature [24]. Therefore, twinning can be formed in all the coatings we prepared according to the calculation, which is in accordance with our experiment.

4. Conclusions

In summary, the mechanical properties of the samples were measured with nanoindentation equipped with SEM in-situ. The hardness of coatings is higher than that of substrates, both in Sample-700 and Sample-250. This increase in hardness can be attributed to the formation of nanoscaled deformation twins in the coatings. Twins restrict the dislocation mobility and serve as nucleation sites for new dislocations. Nanoscaled twins imply a great increase of twin density comparing with the annealed twins in substrates, which results in the high hardness of coatings. Twin boundary is confirmed to be $(11\bar{1})$ plane, and the orientation relationship between the plates is determined to be $(11\bar{1})_M \| (11\bar{1})_T$ and $(\bar{1}10)_M \| (101)_T$. However, the misorientation angle of the deformation twin boundaries in the coating is slightly deviated from 60°. Though the slight deviation of misorientation angle exists, the deformation twins still significantly increase the hardness of the coating, due to its tiny thickness with dimension of several nanometers to hundreds of nanometers. Therefore, the appearance of deformation twins in cold sprayed Cu coatings indicate the cause of the work hardening, and the increase of coating hardness prepared by cold spray provides a new way to make coatings or deposit bulk Cu with high mechanical property if carefully controlled.

Acknowledgements

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