COLD ROLLING OF BULK NANOCRYSTALLINE COPPER

L. LU‡, M. L. SUI§ and K. LU†‡
Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, People’s Republic of China

( Received 22 February 2001; received in revised form 7 June 2001; accepted 7 June 2001 )

Abstract—By means of the electrodeposition technique, a bulk nanocrystalline (nc) copper sample was prepared with a high purity and a high density. The nc Cu sample was found to exhibit extreme extensibility under rolling at room temperature [Science, 287 (2000) 1463]. In this paper, the microstructure evolution of the nc Cu during the cold-rolling process was examined by means of X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). It was found in the initial stage of cold rolling that the microstrain and grain boundary energy increase substantially, while the crystallite size remains unchanged during the whole process. When the degree of deformation exceeds 1000%, the microstrain and the grain boundary energy tend to saturated values, implying that this deformation process is dominated by grain boundary activity rather than lattice dislocation. This phenomenon agrees well with the observed mechanical behavior of the nc Cu sample.

Keywords: Copper; Cold working; Deformation mechanism; Structural behavior

1. INTRODUCTION

The mechanical properties and deformation mechanisms of nanocrystalline (nc) materials have attracted substantial research in recent years [1–3]. Owing to the ultrafine microstructure, nc materials are expected to exhibit superior mechanical properties compared with their coarse-grained counterparts, such as higher strength, more ductility and less strain-hardening effect. The deformation behavior and microstructure development in the nc material can be very different from those in conventional materials [4–6]. These features, on one hand, are extremely interesting for extending our fundamental understanding of the structure–property relationship of materials when the structural modulation scale is reduced into the nanometer regime. On the other hand, the unique properties of nc materials may offer a wide range of technological applications in modern industries.

Nevertheless, the progress is slow in experimental investigations on the mechanical properties and deformation mechanisms in nc materials. One of the major obstacles is the preparation of the nc sample, during which various artefacts are introduced. These artefacts, such as porosity, contamination, residual stress, etc., have significant effects on the mechanical performance [7]. Usually, it is difficult to distinguish the intrinsic nanostructure effect on the mechanical properties as well as the underlying deformation mechanism from the observed mechanical behavior in which those artefacts may play an important role. In order to identify the intrinsic mechanical properties of the nc materials and to exclude the influence of various artefacts, preparation of an “ideal” nc sample is highly desired, i.e., flaw-free, contamination-free, residual-stress-free and with a sufficiently large sample size for mechanical testing.

Recently, we succeeded in synthesizing a bulk and fully dense nc pure copper sample by means of the electrodeposition technique, in which no residual stress exists and the microstrain is negligible. Preliminary tests indicated that this nc Cu sample exhibits some unique mechanical properties. For example, it possesses extreme extensibility during cold rolling at room temperature without work hardening [8]; a significant creep rate was observed in the nc Cu around room temperature [9]; and the tensile ductility is much larger than that in other nc Cu samples prepared by means of consolidation of ultrafine powders [10].
In order to reveal the intrinsic deformation mechanism of the nc Cu, the deformation processes and microstructure evolution in the rolled nc Cu have been investigated intensively in this work. The structure features were monitored by means of X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and thermal analysis. It is suggested that the deformation process of the nc Cu sample is attributed to grain boundary activities rather than lattice dislocations.

2. EXPERIMENTAL PROCEDURES

The nc copper sample was synthesized by means of the electrodedeposition technique [11, 12] with an electrolyte of CuSO₄. The nc Cu sheet (with a thickness of about 1.5 mm) was deposited on a substrate of Ti. The purity of the Cu cathode was about 99.99 wt%. The current density in the present electrodeposition process was about 13 mA/cm². The current density was about 99.98 at%. The sample density was 0.03 g/cm³, which is equivalent to 99.993 at%. The total oxygen content in the as-deposited nc Cu sample was determined by analysis using a LECO TC-436 Oxygen/Nitrogen Determinator, being about 24°. Sodium chloride and gelatin were selected as bath additions with a moderate ratio.

Chemical analysis of the as-deposited nc Cu indicated that purity (exclusive of oxygen) was better than 99.993 at%. The total oxygen content in the as-deposited nc Cu sample was determined by analysis using a LECO TC-436 Oxygen/Nitrogen Determinator, being about 24±1 parts per million (taking oxygen into account, the purity of the as-deposited nc Cu sample is about 99.98 at%). The sample density was measured by means of Archimedes’ principle and was found to be 8.91±0.03 g/cm³, which is equivalent to 99.4±0.3% of the theoretical density for pure Cu (8.96 g/cm³). The nearly full density of the as-deposited nc Cu sample was verified by positron annihilation spectroscopy measurements, which showed that the sample contains no vacancy-cluster-like volumes and no missing crystallites.

The microstructure of the sample was characterized by means of XRD analysis and HRTEM observations. Quantitative XRD measurements of the nc Cu samples were carried out in a Rigaku D/max 2400 X-ray diffractometer with Cu Kα radiation. X-ray wavelengths $\lambda_{K\alpha} = 1.54056$ Å and $\lambda_{K\alpha} = 1.54439$ Å were selected by using a graphite monochromator. The average grain size and microstrain were determined in terms of the diffraction-line broadening of seven single Bragg reflection peaks—(111), (200), (220), (311), (222), (400) and (331)—according to the Scherrer and Wilson method [13]. The (111)/(222) and (200)/(400) peak pairs were used to estimate the microstrain in (111) and (100) planes ($e_{111}$ and $e_{100}$), respectively. Calibration of the instrumental line broadening was performed by using the standard SiO₂ sample. TEM experiments were performed on a JEM 2010 high-resolution transmission electron microscope at an operating voltage of 200 kV. The thin foils for TEM observations were prepared by means of electrochemical polishing at about −20°C. The average grain size of the as-deposited nc Cu sample determined by XRD analysis was about 28 nm, and the mean microstrain was about 0.03%. HRTEM observations indicated that the as-deposited sample consists of ultrafine crystallites (or crystalline domains) with sizes ranging from a few nanometers to about 80 nm. The average grain size is about 20 nm, which is close to the XRD result. Most of the nanometer-sized crystallites are separated by small-angle grain boundaries (with misorientation angles of 1–10°) [8].

Differential scanning calorimetry (DSC; Perkin–Elmer Pyris 1 instrument) was used to study the thermal characteristics of the nc Cu samples. The sensitivity of the energy measurement was about 0.01 mJ/g; the temperature of the calorimeter was calibrated by using pure In and Zn standard specimens, with an accuracy of ±0.02°C. Aluminum pans were used for both the sample and the reference. The nc Cu samples were sealed in aluminum pans and heated in a flowing argon atmosphere at a constant heating rate of 5°C/min. The baseline for DSC curves was determined by reheating the sample at the same heating rate.

Plastic deformation of the as-deposited nc Cu sample was performed by means of cold rolling at room temperature, which resulted in a continuous increase in the sample length in the direction of rolling. The degree of deformation (ε) of the cold-rolled nc Cu sample was defined by $\varepsilon = (d_0 - d)/d_0$, where $d_0$ is the initial thickness of the nc Cu sample and $d$ is the final thickness of the sample after rolling. The strain rate during rolling was controlled to be around 1×10⁻³ to 1×10⁻² s⁻¹. With the progress of repeated rolling, the nc Cu sample became a uniform, long and thin ribbon with smooth surfaces and straight edges, and the final thickness of the ribbon was about 20 μm. The maximum degree of deformation can be as much as 5100% [8]. Such extreme extensibility of the nc Cu sample has not been observed in the conventional coarse-grained polycrystalline Cu, which usually breaks after an extension of about 800%.

3. RESULTS AND DISCUSSION

3.1. Structure characterization

Figure 1 shows the X-ray diffraction patterns for the as-deposited nc Cu and the as-rolled nc Cu specimens with $\varepsilon = 2300\%$. By comparing the relative peak intensities of the seven Bragg reflections in both samples with those for coarse-grained Cu (annealed), different textures were observed. It is seen that the as-deposited nc Cu exhibits an evident (111) texture while no obvious texture is found in the as-rolled sample. The Bragg reflections of the samples exhibit significant broadening. According to the physical broadening profiles, we obtained an average grain size of 28 nm and a mean microstrain of about 0.14% in the as-rolled nc Cu ($\varepsilon = 2300\%$). This means that,
after cold rolling, the microstrain in the nc Cu is greatly elevated, but the average grain size remains unchanged.

The average grain size measured from the X-ray diffraction-line broadening remains unchanged during the whole process, being about 28 nm, as illustrated in Fig. 2. However, the microstrain in the cold-rolled nc Cu samples varied significantly. Figure 3(a) shows the mean microstrain ($\varepsilon$) and the microstrains in (111) and (100) planes ($\varepsilon_{111}$ and $\varepsilon_{100}$) for the nc Cu samples as a function of the degree of deformation. In the early stage of the cold rolling, $\varepsilon_{111}$ increased slightly from 0.06% to 0.1% when the sample was deformed to 500% and then dropped down to zero. It is suggested that the vanishing microstrain in the (111) plane during deformation may be mainly due to the easy dislocation sliding in the (111) plane in Cu with face-centered cubic (fcc) structure. Little change was found in $\varepsilon_{100}$ when $\varepsilon<500\%$. When $\varepsilon>500\%$, $\varepsilon_{100}$ increased slightly from 0.12% to 0.16% and then tended to a saturated value of about 0.16% (when $\varepsilon\approx1000\%$). The mean microstrain increased gradually from 0.03% to 0.16% and then remained unchanged with further deformation.

Cold rolling the conventional coarse-grained Cu under the same conditions, a different scene was observed, as shown in Fig. 3(b): the mean microstrain increased abruptly to about 0.18% and the sample broke at $\varepsilon=800\%$. This corresponds to the work-hardening effect in the coarse-grained Cu during the cold-rolling process in which the lattice dislocation mechanism dominates. Such a microstrain variation in the coarse-grained Cu shows an obvious contrast to that obtained in the nc Cu sample.

In order to examine the microstructure evaluation of the deformation process, a typical TEM image of the cold-rolled nc Cu sample with $\varepsilon=4800\%$ is shown in Fig. 4(a). In the TEM image, Moiré fringes are visible, that originate from nanocrystallites (or crystalline domains) with different crystallographic orientations. According to the modulation wavelength of the fringes, one may estimate the crystallite size as well as the misorientation angles between neighboring nanocrystallites. It is confirmed that in the as-rolled nc Cu there is no obvious grain size change relative to that in the as-deposited one. The statistical misorientation angle distribution determined from the Moiré fringe modulations is depicted in Fig. 4(b). It is found that the misorientation angle of the nanocrystallites is increased clearly from 1–10° (in the as-deposited Cu) to 10–18° in the as-rolled nc Cu specimen, with a mean misorientation of about 13°. This
Fig. 4. (a) TEM observation of the as-rolled nc Cu sample with ε = 4800%; (b) statistic misorientation angle distribution in the as-rolled nc Cu sample in (a).

means that the small-angle grain boundaries are evolved to different grain boundaries with a much larger misorientation, while the average crystallite size remains unchanged during the cold-rolling process of the nc Cu specimen. Or, in other words, a major effect observed to result from the cold-rolling treatment of the as-deposited nc Cu sample is the obvious increment of the grain boundary misorientation angle, or the grain boundary dislocation density, which might be correlated with the obvious increase in the mean microstrain determined from XRD.

3.2. Thermal analysis

The thermal effects in the nc Cu samples with various deformation degrees were investigated by means of DSC in the temperature range between 50°C and 250°C at a constant heating rate of 5°C/min, as shown in Fig. 5. No visible thermal (exothermic or endothermic) effect was detected when the sample was heated further up to 500°C. After the DSC scan up to 250°C, no oxidation was observed in the nc Cu samples. When the as-deposited nc Cu sample was heated, a rather weak exothermic signal was observed in the DSC curve at about 150°C (Tg), of which the integrated enthalpy is about 0.05 J/g. In order to explore the origin of the exothermic heat release in the DSC runs, various as-deposited nc Cu samples were annealed at different temperatures (heated at a rate of 5°C/min to the annealing temperature and cooled down immediately to room temperature by using DSC). The average grain size and microstrain were determined after each annealing process by means of quantitative XRD. The results from the measurements are summarized in Fig. 6. From Fig. 6(a), one can see that no obvious grain growth occurs below 75°C. In the temperature range from 75 to 200°C, the average grain size increased from 30 nm to 80 nm. With a further increase of the annealing temperature (from 200 to 300°C), the average grain size tends to a saturated value, approximating 80 nm. This means that no significant grain growth process occurs between 200 and 300°C.

Figure 6(b) shows the mean microstrain (ε) and the microstrain in (111) and (100) planes, ε_{111} and ε_{100}, in the nc Cu specimens as a function of the annealing temperature. In the as-deposited sample, ε_{100} is much higher (0.13%) than ε_{111} (about 0.08%) and the mean value (ε) from different crystallographic planes (~0.03%). Almost no change was found in the microstrain when the sample was annealed up to 75°C. Above 75°C, an evident drop was observed in ε_{111}, while slight changes were seen in ε_{100} and ε. ε_{100} and ε drop to essentially zero within a narrow temperature range (150–170°C). This confirmed that the exothermic signal within a narrow temperature range (140–160°C) in the DSC curve originated from a microstrain release process in the (100) plane and the mean microstrain.

It is known that the exothermic energy during grain growth can be expressed by [14]:

$$\Delta H = \gamma \left( \frac{1}{d} - \frac{1}{d_0} \right),$$  \hspace{1cm} (1)

where γ is the grain boundary energy, d_0 is the initial average grain size, d is the grain size after annealing.
and \( c \) is a constant dependent on the weight and density of the sample. For example, in our experiment where the sample mass is about 30 mg, one may calculate the total excess enthalpy of a grain growth process. When the grain grows from 37 nm (125°C) to 70 nm (175°C), the enthalpy release per unit time is about 0.0143 mW in the present nc Cu sample with small-angle grain boundaries (taking a sample density of 8.91 g/cm\(^3\) and \( \gamma = 0.1 \) J/m\(^2\)). The critical accuracy of the energy measurement is about 0.01 mW for the current calorimeter (Perkin–Elmer DSC, Pryis 1). Therefore, the thermal effect of grain growth in this as-deposited nc Cu sample is too weak to be detected by the calorimeter. This also means that thermal signals in the DSC measurements of the present nc Cu sample originate mainly from the strain release process.

For the as-rolled nc Cu samples, a clear exothermic reaction was observed. With an increase in the degree of deformation, the exothermic reaction shifts to lower temperatures. The exothermic reaction for the as-rolled samples may be attributed to the microstrain release process and the grain growth process as well, which was confirmed by XRD results [15].

The thermal effect observed in the as-rolled nc Cu is very different from that in the deformed coarse-grained Cu. A comparison of DSC signals between the nc Cu and the conventional coarse-grained polycrystalline Cu with the same \( \varepsilon \) (800%) is shown in Fig. 7. It is evident that a strong exothermic reaction was detected in the as-rolled nc Cu within a temperature range from 128°C \( (T_{\text{on}}) \) to 154°C \( (T_{\text{end}}) \), of which the integrated enthalpy (or enthalpy release) was about 0.93 J/g. But for the as-rolled coarse-grained Cu sample, no thermal effect can be detected in the measured temperature range (up to 500°C). It is evident that the stored energy in the nc Cu induced by plastic deformation is larger than that in the coarse-grained Cu specimens.

The variation of the characteristic temperature as a function of the degree of deformation in the nc Cu is shown in Fig. 8. It is noted that, in the very beginning, the deformation process leads to a fast decrease of the onset and peak temperatures. With further cold rolling, both temperatures tend to saturation values of 140°C to 120°C, respectively. The total decrease is as large as 50°C for the peak temperature and 35°C for the onset temperature. Such a large difference in

![Fig. 6. Variation of (a) the average grain size and (b) the microstrain (as indicated) with annealing temperature for the as-deposited nc Cu sample, determined by means of XRD measurements.](image)

![Fig. 7. DSC curves of the deformed nc Cu and the coarse-grained (CG) Cu with the same degree of deformation (800%), at a heating rate of 5°C/min.](image)

![Fig. 8. Characteristic temperatures (the peak temperature, \( T_p \), and the onset temperature, \( T_{\text{on}} \), of the exothermic DSC peak) as a function of the degree of deformation in the as-rolled nc Cu samples.](image)
the instability temperature implies a remarkable change in the microstructure of the as-rolled nc Cu samples. The saturating instability temperatures indicate that, when $\varepsilon>1000\%$, the microstructure of the as-rolled nc Cu specimens tends to a stable state during the cold-rolling process. No further structural evolution may be activated by plastic deformation.

Similar deformation degree dependencies have been observed with respect to the heat release ($\Delta H$) and the grain boundary enthalpy ($\gamma$). Figure 9 shows the measured heat release as a function of the degree of deformation in the nc Cu. It is obvious that the heat release increases significantly at the initial stage of rolling and tends to a saturated value of about 0.94 J/g when $\varepsilon>1000\%$.

It is noticed that the heat release in the nc Cu specimens is only a small fraction of the heat of fusion ($\Delta H_f$) (about 0.45% $\Delta H_f$ for the as-rolled nc Cu with $\varepsilon\approx5100\%$). This value is much smaller than those reported in the literature. Gunther et al. [16, 17] reported $\Delta H = 2.4\% \Delta H_f$ in an nc Cu with grain size of 40 nm, which was made by consolidation of ultrafine powders. Fecht et al. [18] and Eckert et al. [19] obtained $\Delta H$ as high as 39% $\Delta H_f$ in ball-milled nc Cu with a grain size of 20 nm. In a submicrom crystalline Cu produced by severe plastic deformation, in which the grain size is about 210 nm, the heat release was found to be about 2% $\Delta H_f$ [20]. The difference between our measured results and the literature data may be attributed mainly to the difference in grain boundary structures. In both the consolidated nc samples and the ball-milled ones, high-angle grain boundaries with random crystallite orientations are formed. These grain boundaries typically have high grain boundary energy with a high density of grain boundary defects. For the sample processed by severe plastic deformation, the grain boundary energy is also high due to the high density of grain boundary defects. However, for our nc Cu sample, as indicated by structure characterization, most grain boundaries are of small angle with a mean misorientation of about 13°. Therefore, these grain boundaries have a small excess enthalpy. Meanwhile, other unknown differences in the structure of the nc samples, which were produced by means of different methods, may be also responsible for the difference between the present measured results and the literature data.

### 3.3. Grain boundary enthalpy

During a grain growth process in an nc material from an initial grain size of $d_0$ to a final size of $d$ (supposing that the grain morphology does not change during grain growth), the total grain boundary area in the sample will be deduced by:

$$\Delta S_{gb} = \frac{3W}{2D(d_0 - d)},$$  \hspace{1cm} (2)

where $W$ is the sample weight and $D$ is sample density. Here the sample is assumed to be spherical and the grain boundary thickness is assumed to be 1 nm.

Supposing no shape change of the crystallites takes place and the grain boundary enthalpy $\gamma$ remains unchanged during the grain growth process, the stored energy concentrated at the grain boundaries, one may get the grain boundary enthalpy from the heat release during the grain growth process by:

$$\gamma = \frac{\Delta H_{gg}}{\Delta S_{gb}}.$$  \hspace{1cm} (3)

XRD results indicate that, during the grain growth process, the average grain size of the nc Cu samples was increased from 30 nm (initial grain size) to about 80 nm (final grain size up to 250°C) [15]. Thus the grain boundary enthalpy can be estimated according to equation (3). Figure 10 shows the resultant grain boundary enthalpy for the nc Cu samples as a function of the degree of deformation. It is obvious that the grain boundary enthalpy of the as-deposited nc Cu was small, only about 0.012 J/m². The grain boundary enthalpy increased gradually in the initial deformation process and tended to saturate at a value of about 0.27 J/m² when $\varepsilon>1000\%$.

From the TEM observations, we noticed that most
of the nanometer-sized crystallites in the as-deposited nc Cu sample were separated by small-angle grain boundaries. After cold rolling, the mean misorientation angle of the crystallites was increased to about 13°, which was still in the range of the small-angle grain boundaries. Based on the tilt dislocation model, the small-angle grain boundary (θ<15°) energy (γgb) is related to the misorientation (θ) by [21]:

\[ \gamma_{gb} = E_0 \theta (A_0 - \ln \theta). \]  

(4)

Where \( E_0 \) and \( A_0 \) are related to the elastic strain energy:

\[ E_0 = \frac{\mu b}{4\pi(1-\nu)} \quad \text{and} \quad A_0 = 1 + \ln\left( \frac{b}{2\pi r_0} \right), \]

(5)

where \( \theta \) is the misorientation angle of the crystallites, \( \mu \) is the shear modulus, \( b \) is the Burgers vector, \( \nu \) is Poisson’s ratio, and \( r_0 \) is related to the core energy of a single boundary dislocation.

Taking the relevant parameters from the literature for Cu [22], one may get an estimated value of grain boundary energy of 0.30 J/m² for \( \theta = 13^\circ \). The resulting value of \( E_{gb} = 0.27 \) J/m² from DSC measurements is in reasonable agreement with the literature data.

From the variation tendencies of grain boundary enthalpy (as shown in Fig. 10) and the microstrain [Fig. 3(a)] with the degree of deformation in the nc Cu, one may find that the cold-rolling process can be divided into two stages in which the deformation mechanism may be proposed as follows.

- **Stage I:** \( \varepsilon < 1000\% \). In this stage, the deformation process seems to be dominated by dislocation activities (probably in large grains or at the grain boundaries). Generation and motion of dislocations may result in a substantial increase in the density of defects (i.e., the microstrain) and in the misorientation between neighboring grains due to the pile-up of dislocations at grain boundaries. Hence the grain boundary energy increases in this stage. This tendency can also be verified by the results of hardness measurements, which show a slight hardening effect during this stage [8].

- **Stage II:** \( \varepsilon \geq 1000\% \). The microstrain, grain boundary enthalpy and grain boundary structure, as well as the grain size, remain unchanged in this deformation stage. Also, the hardness of the nc Cu sample becomes constant when \( \varepsilon \geq 1000\% \) [8]. This implies that lattice dislocation activity is no longer a dominating mechanism in the deformation. Instead, grain boundary activities (grain boundary sliding or grain boundary diffusional creep) may be activated and become dominant in the deformation as the grain boundary structure is evolved to be of higher energy (with a higher density of defects). When the deformation is controlled by grain boundary activities, the strain-hardening effect disappears [8], and grain boundary structure as well as the dislocation density tends to be saturated. Such a two-stage behavior in the nc Cu during cold rolling has also been verified in the variation of the electrical resistance with the degree of deformation [25].

Grain boundary energy is determined by the grain boundary structure. In nc materials, microstrain, which is a signature of density of defects, is closely related to the grain boundary structure. Therefore, it is reasonable to correlate the grain boundary energy with the microstrain in nc materials. From our measurement results, we noticed that with an increase of the degree of deformation, the grain boundary energy increases, accompanied by an increment of microstrain. Figure 11 is a plot of grain boundary enthalpy determined by DSC as a function of measured microstrain (from XRD) for the nc Cu specimens. The literature datum of grain boundary energy in the inert-gas-consolidated (IGC) nc Cu is also included [15, 16]. Evidently, it turns out that \( \gamma \) increases with the microstrain in an approximately linear relation.

Such a correlation between the grain boundary energy \( \gamma \) and the microstrain might imply that most defects in the nc Cu, including point defects and dislocations, are associated with the large amount of grain boundaries. Especially for the deformed nc samples (including as-rolled and consolidated), the high density of dislocations induced by deformation might be concentrated on grain boundaries so that the excess energy of grain boundaries is closely related to the density of dislocations. The higher the density of dislocation manifested by a higher microstrain, the larger the grain boundary excess energy will be.

![Fig. 11. Plot of the grain boundary energy versus the mean microstrain in different nc Cu samples (as-deposited, as-rolled and inert-gas-consolidated (IGC) [16, 17]) with an average grain size of about 30 nm.](image-url)
4. CONCLUSIONS

The microstructure evolution during the cold-rolling process of an electrodeposited nc Cu sample was investigated. In the initial stage of cold rolling ($\varepsilon<100\%$), the deformation is dominated by dislocation activities, resulting in a substantial increase in the microstrain (density of defects) and grain boundary energy. No obvious change was found in the crystallite size during the whole process. In the late stage of rolling ($\varepsilon\geq100\%$), the microstrain and grain boundary energy tend to saturated values, implying that the deformation process is dominated by grain boundary activities rather than lattice dislocations. This trend is consistent with the measured mechanical behavior in the nc Cu sample.

Acknowledgements—Financial support from the National Science Foundation of China, the Ministry of Science and Technology of China (Grant G1999064505) and the Max-Planck Society of Germany is acknowledged.

REFERENCES

23. Lu, L., et al., manuscript to be published.