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ARTICLE

Experimental Investigation on the Correlation Between Pop-in and Vacancy Activities of High-Entropy Alloy CoCrFeMnNi

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Abstract: With the advancement of nanoindentation technology, more and more data support that the pop-in event is not a homogeneous but a heterogeneous dislocation nucleation process mediated by vacancy-like defects. However, the conclusion is based on the two model-extracted parameters, namely activation energy and activation volume. Few experiments can directly correlate the pop-in event with vacancy activities. Following our previous nanoindentation study on fcc high entropy alloy CoCrFeMnNi, this correlation was verified by specially-designed nanoindentation experiments. Results show that when the indenter is held under a subcritical load (in reference to the critical load that triggers instantaneous pop-in) for a period of time, delayed pop-in is observed. Furthermore, the displacement bust size increases with the tip radius up to a few hundred nanometers. These two observations suggest that the vacancy is at play because the vacancy can migrate under any applied stress and its number within the indented volume depends on the tip radius.

Key words: nanoindentation; pop-in; dislocation nucleation; vacancy; time dependence; tip radius dependence

Pop-in, defined as the displacement burst during load controlled nanoindentation, marks the transition from elastic to plastic deformation, which is also called the incipient plasticity or the onset of plasticity. Since pop-in typically occurs at a depth of 10~20 nm or less, the indented volume is small and it is very likely to avoid any pre-existing dislocations, that is, the carrier of plasticity. Therefore, it can be attributed to the dislocation nucleation[1]

Early on, most researchers on the basis of atomic simulations believed that the pop-in event is governed by the homogeneous dislocation nucleation from perfect lattice. For example, Li et al[1] conducted atomic simulations on <111> single crystal Al and found that the stress required to initiate the pop-in reaches 5.5 GPa, almost one fifth of its shear modulus, and they concluded that the pop-in is caused by the homogeneous dislocation. Similar argument was made on the <111> Au[2]. Later, with the advancement of experimental techniques such as high temperature nanoindentation test and the use of statistical model[3-6], more and more quantitative experimental data are now available and suggest that the pop-in event is a heterogeneous dislocation nucleation process mediated by vacancy-like defects. For example, Schuh et al[4] developed a statistical model to assess the loading rate and temperature dependence of pop-in and extracted the activation volume and activation energy for single crystal Pt as 0.5 Ω (Ω: one atomic volume) and 0.3 eV, respectively. Zhu et al[7] adopted Schuh's model and obtained the activation volume and energy for a face-centered cubic high entropy alloy CoCrFeMnNi, namely 3 Ω and 1.75 eV, respectively. Ye et al[8] investigated the pop-in behavior in body-centered cubic high entropy alloy HfZrTiNb with Schuh's model and found that the activation volume is 3~5 Ω. These values are in good agreement with those of a vacancy[9], suggesting that pop-in is a heterogeneous dislocation nucleation process with vacancies involved instead of homogeneous dislocation nucleation which will require at least tens or hundreds of atoms moving

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altogether and thus much higher activation volume and energy[10].

However, the conclusion that pop-in is a heterogeneous dislocation nucleation process with the aid of vacancy is singly based on the evaluation of two model-extracted parameters, namely activation volume and activation energy. There are hardly any experiments that can directly link the pop-in with vacancy activities. Following our previous work on nanoindentation of a high entropy alloy CoCrFeMnNi[7], this research aims to validate this linkage through specially-designed nanoindentation experiments.

If the conclusion is true as asserted, that is, the vacancy is responsible for the pop-in, then the factors affecting the vacancy activities will reflect in the pop-in behavior. So the experiments can be designed behind the following reasoning. First, if the sample is held at a subcritical load (in reference to the critical load that triggers instantaneous pop-in), the vacancy will still migrate, as it will migrate under any applied load, into a cluster for creating a critical dislocation loop nucleus. But this process requires migration time and thus leads to the time dependence of the pop-in behavior. Second, if the nanoindenter tip radius is varied, the indented volume along with the number of vacancy sites included in the volume will be different. While the number of vacancy sites determines the number of dislocation nucleated, and it in turn determines the size of pop-in or the displacement burst, which is defined as the displacement difference between the start and the end of pop-in. So the size of pop-in will be proportional to the indenter tip radius. Essentially, the validation of the conclusion is simplified to two questions: whether the sample held under a subcritical load still shows pop-in after a period of holding time, and whether the size of displacement burst scales with the tip radius.

1 Experiment

The sample used in this study was the same as our previous work[7] with the microstructure shown in Fig.1. Nanoindentation experiments were performed using a Hysitron Triboindenter (Hysitron, Inc. Minneapolis, MN). Previously, it was found that the average critical load for 121 indentations to trigger instantaneous pop-in at room temperature is 420 μN with a tip radius of 638 nm[7]. Using this tip, five tentative subcritical loads of 320, 280, 240, 200 and 160 μN were applied to the sample with a 50 s holding time and 5 s for each loading and unloading segment. For every load, 25 indentations were made within one grain. Later, a smaller tip with a radius of 233 nm was used to accommodate more indentations within one grain, to obtain more statistical data. As the tip radius decreased, the level of subcritical load was lowered accordingly. Four different loads, 125, 150, 175 and 200 μN with an increment of 25 μN, were selected and 200 indentations were performed on a separate grain under each load to identify the statistical trend. The loading function was also three-staged, consisting of 5 s loading, 50 s holding and 5 s unloading.

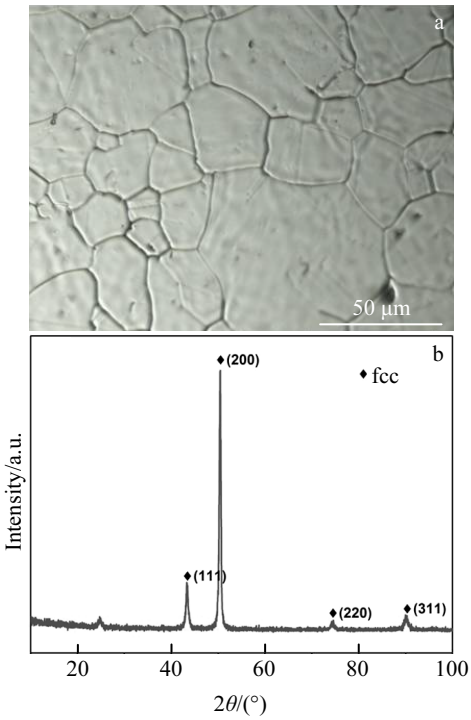

Fig.1 OM image (a) and XRD pattern (b) of fcc crystal structure

To examine the tip radius effect, four different diamond indenter tips were used with an effective radius of 105, 233, 467 and 638 nm. The radius was calibrated using the standard procedure[11,12]. 25 indentations were made for each radius on a separate grain and all the indentations were performed using the same loading function.

2 Results and Discussion

2.1 Time dependence

For 25 indentations at 320 μN, 3 of them exhibited reversible loading and unloading; 10 have pop-in prior to holding; and 12 have pop-in during holding. For indentations at 280 μN, 19 indentations show pop-in during holding and 6 indentations show completely elastic. Typical load-depth profiles are represented in Fig.2a and 2b.

It can be seen that the pop-in occurs after a period of incubating time, which is consistent with the observations reported in Fe-3%Si[13] and Ni3Al[14,15]. For 240 μN and below, there is no delayed pop-in during holding (Fig.2c), indicating that there is a threshold stress for germinating pop-in or the holding time window may be too small as the pop-in has been delayed for more than 600 s in Ni3Al[14].

To examine the statistics of the pop-in behavior under different subcritical loads, a much smaller tip was used to accommodate as many as 200 indentations in one grain. Fig.3 shows the histogram of those delayed pop-in, in which the vertical and the horizontal axis stand for the number of counts

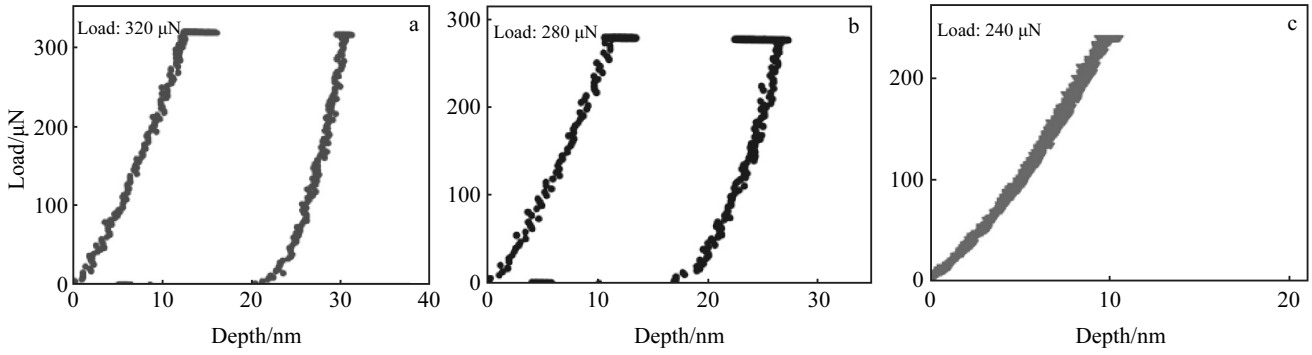

Fig.2 Load-depth profile under different subcritical loads: (a) 320 μN, (b) 280 μN, and (c) 240 μN

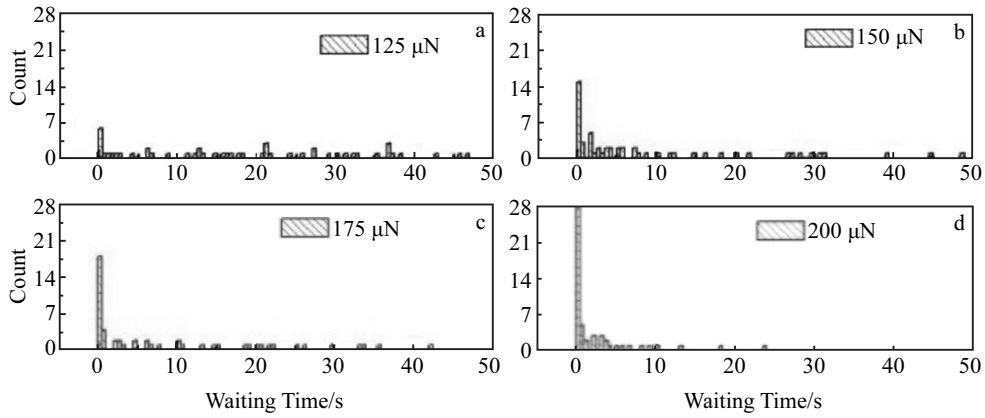

Fig.3 Waiting time histogram of delayed pop-in under different holding loads: (a) 125 μN, (b) 150 μN, (c) 175 μN, and (d) 200 μN

and the waiting time needed before pop-in, respectively. It can be seen that with increasing the load, more and more indentations show pop-in and the average waiting time gradually becomes shorter. However, the deviation of average waiting time is even bigger than the average waiting time itself. This statistical anomaly can be explained by the random-walking nature of the vacancy migration (Brownian motion).

2.2 Tip radius dependence of the pop-in behavior

Representative load-depth (*P*-*h*) curves for various radii are shown in Fig.4 and the pop-in is clearly observed in each curve. The pop-in size, which is defined as Δh in Fig.4, is measured to be 2.1±0.5, 14.3±2.5, 23.6±2.8, 27.6±2.2 nm for radius of 105, 233, 467, and 638 nm, respectively. Fig.5 plot the pop-in size as a function of the tip radius[16]. Apparently, the pop-in size increases with the tip radius.

According to the transition state theory, the nucleation rate at which a critical event (for example, formation of the critical nucleus) occurs can be described in Arrhenius form:

$$n_c = n_o v \exp(-\frac{H-\sigma V}{RT}) \quad (1)$$

where n_c is the number of critical nucleation nucleus formed per second, n_o is the available nucleation sites in the stressed volume, v is the attempting frequency factor on the order of Debye frequency, H is the enthalpy, σ is the applied stress, and V is the activation volume.

The population of nucleation sites n_o, which is vacancy, can be estimated as follows. As the sample is fully annealed, its equilibrium concentration of vacancy at room temperature is around 10^{-6} [17]. When it is brought to nanoindentation, the stressed volume underneath the indenter scales with the contact radius a by πa^3. Therefore, n_o can be expressed as:

$$n_o = 4(-\frac{\pi a^3}{a_o^3}) \times 10^{-6} \quad (2)$$

where a_o is the lattice constant, 4 represents the number of atoms in a fcc unit cell. According to the Hertzian theory[18], the contact radius is correlated with tip radius:

$$a = \sqrt{hR} \quad (3)$$

where h is the pop-in depth and R is the tip radius. They are related through Eq.(4):

$$P = \frac{4}{3} E_r R^{1/2} h^{3/2} \quad (4)$$

where P is the pop-in load and E_r is the reduced modulus of

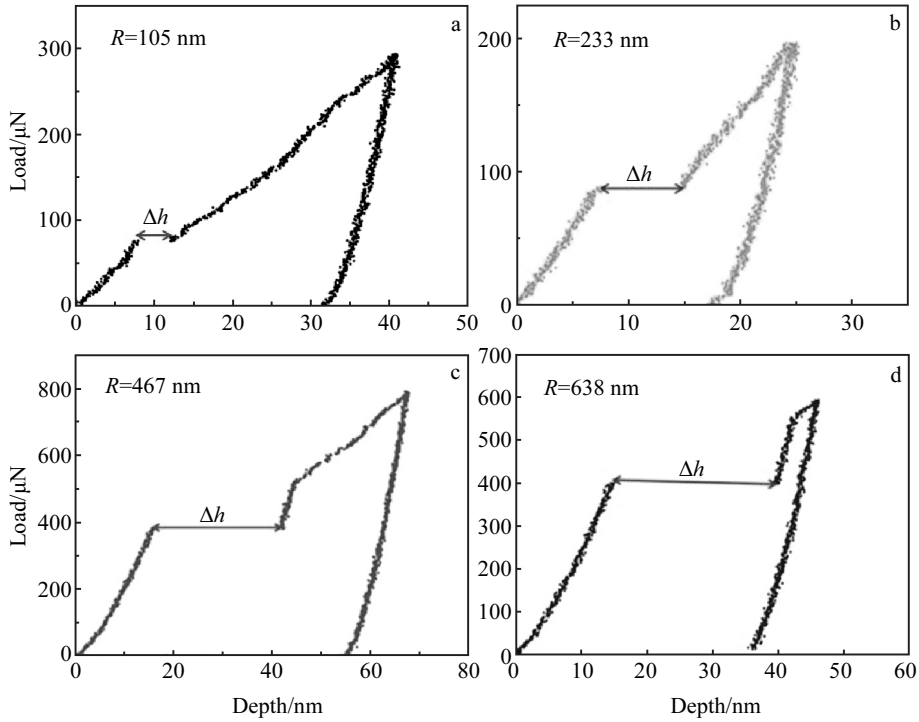

Fig.4 Representative load-depth curves at different tip radii (R): (a) R=100 nm, (b) R=233 nm, (c) R=467 nm, and (d) R=638 nm

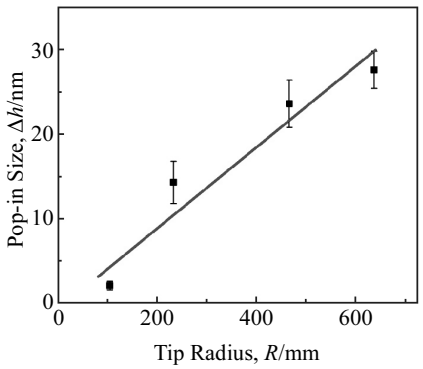

Fig.5 Pop-in size as a function of tip radius

the indenter and sample. Inserting Eq.(3) and Eq.(4) into Eq.(2):

$$n_o = 3\pi \times 10^{-6} \cdot \frac{P}{E_r a_o^3} \cdot R \quad (5)$$

Eq.(5) shows that the vacancy sites are proportional to the tip radius R, consistent with the data shown in Fig.4. This strongly suggests that the increase of pop-in size is associated with the increase of the population of vacancy sites due to increase in stressed volume, indicating that vacancies play an important role in the pop-in event.

3 Conclusions

1) When sample is held under a subcritical load, pop-in occurs after a period of waiting time. This time can be regarded as the time needed for vacancies to migrate via random walking and merge into a vacancy cluster, which can serve as the nucleation site for a critical dislocation loop.

2) When the tip radius increases, the pop-in size also increases. This phenomenon can be well explained by the fact that the number of vacancies contained within the stressed volume is proportional to the number of dislocations nucleated and in turn determines the pop-in size.

3) Both the observation of time dependence and tip radius dependence suggests that the vacancy plays an important role in the pop-in event.

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高熵合金 CoCrFeMnNi 纳米压痕中位移突变现象和空位活动的关联性验证

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摘　要：随着纳米压痕技术的进步，越来越多的数据表明纳米压痕中发生的位移突变现象不是完美晶格均质形核过程而是借助于空位的异质位错形核过程。但是这个结论主要是基于纳米压痕力学统计模型提取的激活能和激活体积这 2 个参数确立的，而鲜有实验直接验证位移突变或位错形核与空位之间的关联。根据先前对高熵合金的纳米压痕研究，通过设计的纳米压痕实验来验证这种关联性。实验发现，当施加的载荷保持在亚临界水平一段时间后，依然可以观察到位移突变；而且，位移突变的大小（位移突变结束和开始时刻的位移差）与纳米压痕的压头尺寸成正比。位移突变对时间和压头尺寸的依赖性可以通过空位的特性得到合理的解释：第一，空位在任何载荷水平下都会发生迁移，而且需要一定时间形成空位堆作为位错的形核中心；第二，空位数量与压头作用区域的体积成正比，而这个体积又与压头尺寸成正比，另一方面，空位数量又决定了位错形核的数量进而解释了位移突变尺寸与压头尺寸成正比的现象。这也就从实验上直接验证了空位在位移突变或位错形核的过程扮演的重要角色。

关键词：纳米压痕；位移突变；位错形核；空位；时间相关性；压头尺寸

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