

非晶合金“拉伸转变区”模型

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2016-04-19 收稿, 2016-05-12 修回, 2016-05-13 接受, 2017-03-07 网络版发表

国家自然科学基金优秀青年科学基金(11522221)、国家自然科学基金(11372315, 11472287)、中国科学院前沿科学重点研究项目(QYZDJSSW-JSC011)和中国科学院战略性先导科技专项(B类)(XDB22040303)

摘要 非晶合金是熔体深度过冷至玻璃态转变, 结构发生突然“冻结”而形成的玻璃态固体. 在远低于玻璃转变温度, 非晶合金的宏观断裂通常由塑性变形局部化剪切带诱导. 尽管非晶塑性机理还未完全揭示, 但普遍认为剪切带模式的裂尖塑性流动源于材料内部原子集团的局部剪切重排, 即“剪切转变区(shear transformation zone, STZ)”事件. 但是, 越来越多的工作表明, 非晶合金的断裂并非总是由剪切带诱导, 而呈现脆性的拉伸正断, 并涌现出一种新的断裂面斑图: 纳米周期条痕. 针对这一全新的断裂能耗散过程, 我们在2008年提出了非晶合金的“拉伸转变区(tension transformation zone, TTZ)”模型. 本文将简要介绍非晶合金“拉伸转变区”模型的提出、内涵本质、激活条件、原子模拟和韧脆转变实验验证等, 并对该模型的未来发展进行评述.

关键词 非晶合金, 剪切带, 断裂, 剪切转变区, 拉伸转变区

在人类能够制备和使用金属的几千年历史中, 块体金属材料总是以晶体状态存在. 20世纪50年代, 美国哈佛大学物理学家Turnbull教授^[1]预言, 液态金属在冷却速率足够高的条件下可发生玻璃态转变而形成非晶态. 1960年, 美国加州理工学院的Duwez教授及其同事^[2]通过发明快速淬火技术, 制备出了Au₇₅Si₂₅非晶合金, 证实了Turnbull的预言. 到20世纪80年代末90年代初, 随着制备思路从急冷工艺改进向合金成分设计的转变, 非晶合金的特征尺度实现了从微米到毫米/厘米的突破^[3,4]. 从此, 非晶合金进入块体时代, 各种体系如雨后春笋般涌现^[5-7], 几乎涵盖了元素周期表中所有金属元素. 非晶合金内部原子排列接近密排堆积, 具有类似晶体结构的短程序甚至中程序^[8,9]. 但是, 短/中程序如何堆积成亚稳的各项同性长程无序的三维结构, 仍然是一个

谜^[10-12]. 尽管如此, 独特的微结构赋予这类合金一系列优异的力学、物理和化学性能, 如高强度、大弹性极限、耐磨损、抗腐蚀、软磁性和大磁熵等, 使其作为先进材料在国防、空天等高科技领域显示出了广阔的应用前景^[13-19].

在远低于玻璃态转变温度, 非晶合金的塑性变形极易局部化, 形成纳米尺度的剪切带^[20-23]; 剪切带的演化往往诱导材料发生剪切主控的断裂, 并呈现典型的微米尺度脉状纹理断裂面形貌^[24-26](图1). 一直以来, 这种由剪切带诱导断裂的材料失效模式被认为决定着非晶合金几乎所有的力学性能, 因此, 受到各领域学者的广泛关注^[27-29]. 尽管精细图像还未完全揭示, 但是普遍认为, 裂纹尖端剪切带模式的塑性流动是材料内部原子集团局部剪切重排一系列时空演化的结果. 美国麻省理工学院的Argon教

引用格式: 蒋敏强, 戴兰宏. 非晶合金“拉伸转变区”模型. 科学通报, 2017, 62: 2346-2357

Jiang M Q, Dai L H. The “tension transformation zone” model of amorphous alloys (in Chinese). Chin Sci Bull, 2017, 62: 2346-2357, doi: 10.1360/N972016-00509

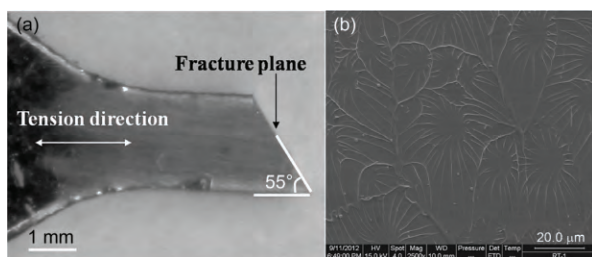


图1 一种典型Zr基块体非晶合金在室温准静态单轴拉伸下的宏观断裂模式(a)和微观断裂面形貌(b)^[24]

Figure 1 Quasi-static uniaxial tension of a Zr-based bulk amorphous alloy at room temperature. (a) Macroscopic fracture mode; (b) microscopic fracture morphology^[24]

授^[30]在1979年将这种原子集团剪切主控的协同重排事件定义为“剪切转变区(shear transformation zone, STZ)^[1]”。从断裂能耗散角度来看,这种由剪切带诱导的断裂本质上是塑性的,微观基本耗散过程是STZ;裂纹的扩展是一种发生在空气(裂纹)和流体(裂尖塑性软化层)界面的弯月失稳^[31]。众所周知,在晶态金属中,除了以位错运动等机制诱导的塑性断裂外,还存在沿着晶面解理的脆性断裂。如果将非晶STZ比拟为晶体位错运动,那么,在非晶合金中是否也存在以形成新表面为主要能量耗散机制的脆性断裂?如果存在,那么基本的微观过程或者机理是什么?这些问题的回答,将极大地挑战人们对于材料变形和断裂的传统认知。

1 非晶合金的脆性断裂

关于非晶合金是否存在脆性断裂这一问题,早在非晶合金薄带年代似乎就已经有了答案。例如, Masumoto和Maddin发现^[32], Pd₈₀Si₂₀非晶合金薄带在室温拉伸条件下能够呈现与传统硅玻璃几乎一样的脆性断裂特征: (1) 断裂面与拉伸轴垂直; (2) 断裂面形貌在光学显微镜下沿着断裂方向依次出现“镜面(mirror)”、“雾状(misty)”和“锯齿(hackle)”三个典型区域。Pampillo和Polk^[33,34]在Fe基非晶合金薄带中也观察到了类似的拉伸正断模式。应用扫描电子显微镜,他们还发现在断裂面上剪切流动痕迹(即图1所示的脉状纹理)彻底消失,取而代之的是一种非常精细在

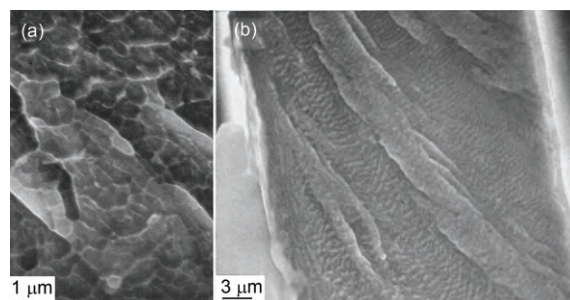


图2 精细涟漪断裂面形貌^[33,34]。(a) Fe₇₆P₁₆C₄Al₃B₁非晶薄带室温拉伸; (b) Fe₃₇Ni₃₇P₁₄B₆Al₃Si₃非晶薄带190 K拉伸

Figure 2 Fine-dimple-like fracture morphologies^[33,34]. (a) Room-temperature tension of a Fe₇₆P₁₆C₄Al₃B₁ amorphous alloy ribbon; (b) 190 K-tension of a Fe₃₇Ni₃₇P₁₄B₆Al₃Si₃ amorphous alloy ribbon

亚微米尺度无择优取向的涟漪(dimple)结构(图2)。Nagendra等人^[35]在La基块体非晶合金的夏比冲击实验中也在断裂面上观察到了这种精细的涟漪结构。尽管如此,非晶合金的拉伸脆断及其断裂面上呈现的精细涟漪结构一直没有引起足够的重视。

直到2005年,中国科学院物理研究所汪卫华课题组通过对一种脆性Mg基块体非晶合金的三点弯断裂面观察,证实在光学显微镜下所谓的“镜面”区实际上就是在扫描电子显微镜下观察到的精细涟漪结构(图3(a))^[36]。此外,该课题组发现涟漪的特征尺度依赖于非晶合金的断裂韧性;当特征尺度小于100 nm时,涟漪结构转变为间距在几十纳米的周期条痕(periodic corrugations)^[37],见图3(b)。很快,在其他脆性非晶合金体系(如Fe基、Co基、Dy基和Ni基等)的I型断裂面上也相继观察到了这种纳米周期条痕结构^[38-41]。

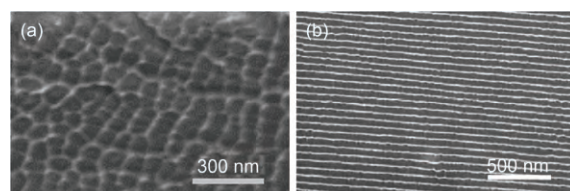


图3 一种脆性Mg基块体非晶合金三点弯断裂面上“镜面”区呈现的百纳米尺度的涟漪结构(a)和纳米周期条痕结构(b)^[36,37]

Figure 3 The mirror-like region on the fracture surface of a brittle Mg-based bulk amorphous alloy under the three-point bending^[36,37], showing 100 nm-scaled dimples (a) and nanoscale periodic corrugations (b)

1) Argon的原始定义为“剪切转变(shear transformation, ST)”。后来Falk和Langer将“剪切转变”发生的潜在区域定义为“剪切转变区(shear transformation zone, STZ)”,并建立了非晶塑性的STZ理论(Phys Rev E, 1998, 57: 7192-7205)。尽管两者原始含义存在本质区别,但是目前已不再区分。两者都描述原子集团协同剪切重排的动态事件。具体可参阅:蒋敏强.非晶合金塑性理论研究进展,中国材料进展,2014,33:257-264

全新断裂形貌的不断涌现使人们开始重新关注“非晶合金的断裂到底是脆性还是塑性?”这个重要问题,并引起领域内的广泛争议.一种观点认为^[36,40,41],非晶合金的断裂本质上还是塑性的,精细的涟漪或纳米周期条痕结构只不过是裂尖塑性流动更加局域化的结果.前者仍然可以用裂纹面的弯月失稳描述;而后者则可理解为在弯月失稳抑制条件下裂纹前端一系列塑性孔洞化导致的.事实上,纳米周期条痕的确呈现峰对峰、谷对谷分离的孔洞化(cavitation)特征^[40].另一种观点则认为^[38,42],纳米周期条痕的形成是由于原子无序导致的波动解理,断裂能耗散机制是新表面形成,而不是局域塑性.但是,这两种观点都存在与实验不一致的地方.如果裂纹尖端是塑性的,那么剪切主控的STZ为什么能引起宏观的拉伸正断?而周期条痕的波动解理解释又与其孔洞化特征相矛盾.

为了澄清这些疑问和矛盾,中国科学院力学研究所戴兰宏课题组针对一种典型锆基(Vitreloy 1)^[4]块体非晶合金,在一级轻气炮装置上开展了高速平板冲击实验^[43].基于样品构型和应力波设计,实现了

Vitreloy 1非晶合金应变率高达 $\sim 10^6 \text{ s}^{-1}$ 的动态I型开裂.他们在断裂面上观察到了许多光滑的区域(图4(a)),这些所谓的“镜面”区在扫描电子显微镜下也呈现出间距约80 nm在空间上周期波动的条痕结构(图4(b))^[24].这是首次在非晶合金的韧性体系中观察到纳米周期条痕,表明这种断裂形貌在非晶合金中具有广泛的普遍性.原子力显微镜观测进一步证实,纳米周期条痕本质上是一系列自组装的纳米尺度孔洞(图4(b)和(d));孔洞的形成区域构成了纳米条痕的波谷,而孔洞之间的连接区域构成了波峰^[44].

为了揭示这些纳米孔洞的形成机制, Jiang等人^[44]采用非趋势涨落分析法对纳米周期条痕的表面轮廓沿着三个特征方向:裂纹扩展、波峰和波谷进行了定量分析,见图5.结果显示,沿着裂纹扩展方向,表面轮廓的波动周期(条痕间距)实际是64 nm,在这个尺度下空间点之间是长程关联的;沿着波峰方向,表面轮廓存在一个32 nm的特征间距,在这个尺度下空间点之间也是长程关联的;但是,沿着波谷方向,表面轮廓不存在特征尺度,空间点之间没有关联性,并且表现出明显的分形特征.基于这些分析,他们揭

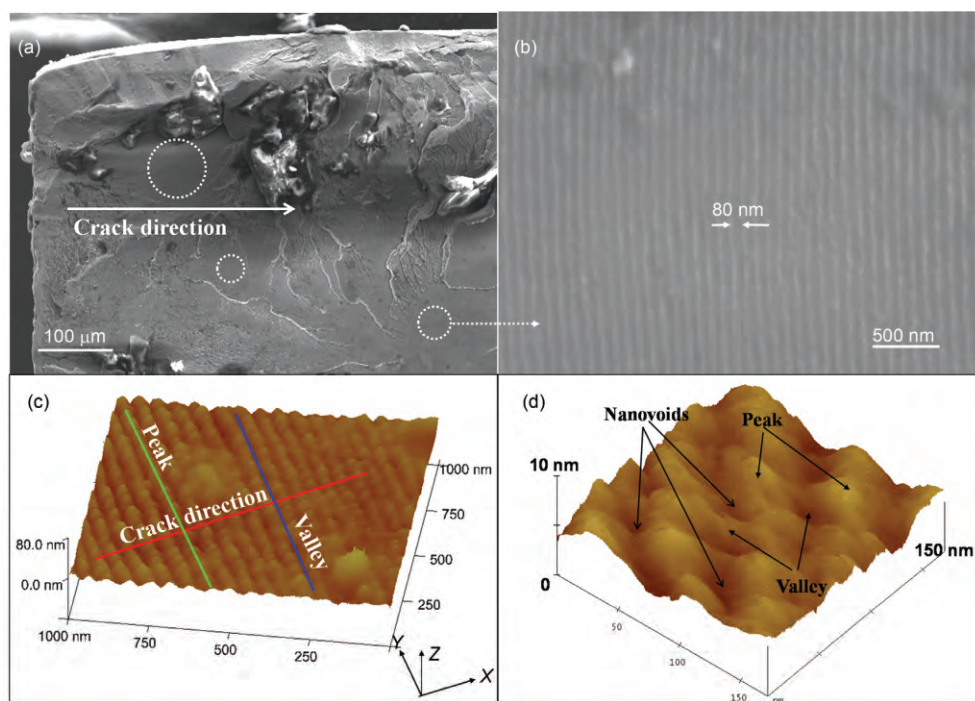


图4 (网络版彩色)一种典型Zr基块体非晶合金动态I型断裂面上“镜面”区呈现的纳米周期条痕在扫描电子显微镜((a), (b))和原子力显微镜下的形貌((c), (d))^[24,44]

Figure 4 (Color online) The mirror-like region on the mode I fracture surface of a typical Zr-based bulk amorphous alloy, showing nanoscale periodic corrugations in SEM ((a), (b)) and AFM ((c), (d))^[24,44]

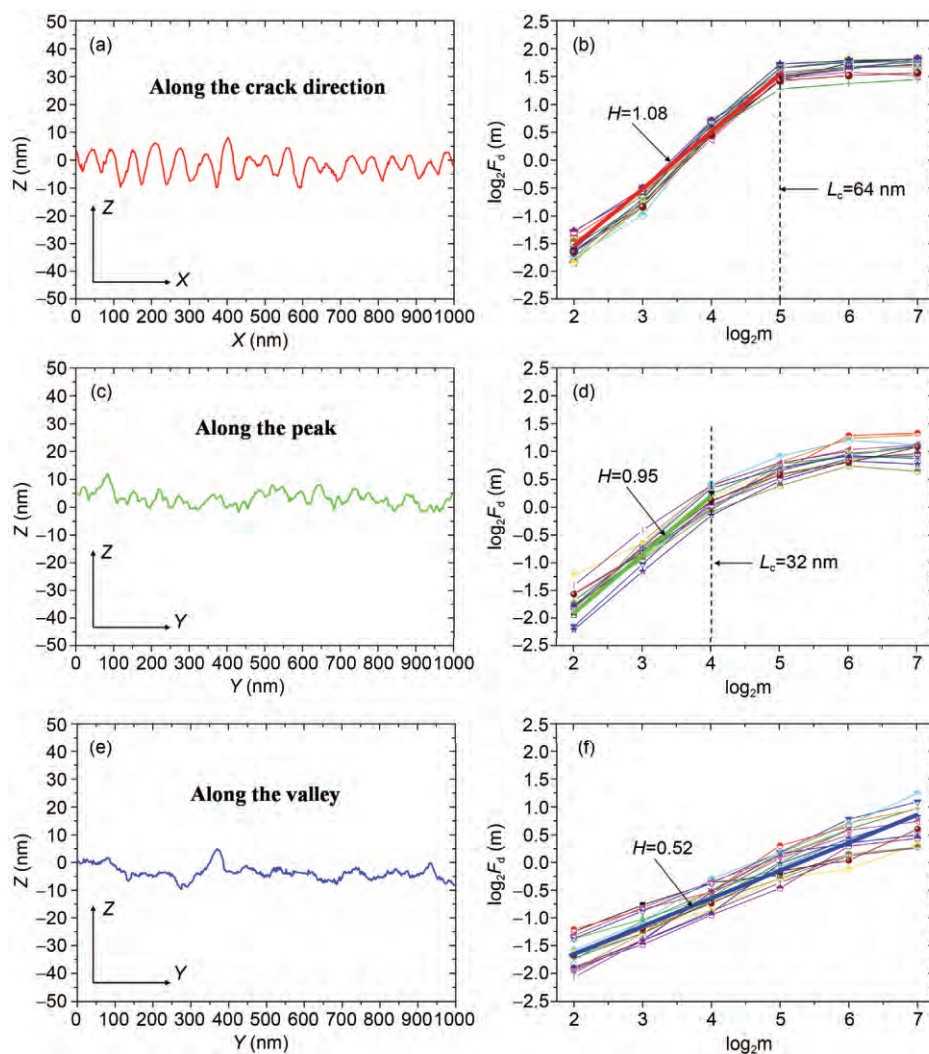


图5 (网络版彩色) 纳米周期条痕表面形貌的非趋势涨落分析^[44]. (a), (b) 沿着裂纹扩展方向; (c), (d) 沿着波峰方向; (e), (f) 沿着波谷方向
Figure 5 (Color online) Representative AFM profiles and the corresponding detrended fluctuation analysis results of the nanoscale periodic corrugations^[44]. (a), (b) Along the crack direction; (c), (d) along the peak and (e), (f) along the valley

示出纳米周期条痕的形成源于以下两个过程的周期性交替^[24,44,45]: 首先, 纳米/亚纳米尺度孔洞在裂纹面前端的瞬时成核; 然后, 这些成核的孔洞通过十分微弱的塑性流动与裂纹面连接贯通, 形成一个新裂纹面. 前一个过程中新表面的快速形成使波谷形貌继承了非晶结构在短中程序固有的分形本质^[11], 而第二个过程中微弱的塑性流动导致波峰形貌在非常有限空间内存在长程关联.

至此, 基本可以确定非晶合金能够发生脆性断裂, 且微观机制是准脆性的纳米尺度孔洞化. 这明确否定了非晶合金脆性断裂的波动解理机制, 也澄清了非晶合金脆性断裂与塑性孔洞化的矛盾.

2 “拉伸转变区”模型

2.1 模型的提出

在原子尺度上, Argon定义的STZ描述了局部原子集团剪切主控的重排事件^[30], 如图6(a)所示. 由于非晶合金内部原子的密排无序堆积, STZ过程中必然伴随着体积膨胀, 即所谓的剪胀效应^[46,47]. 非晶合金宏观剪切变形/断裂所表现出的正应力效应和压力敏感性就源于这种固有的剪胀效应^[25,26,48,49]. 但是, 通常情形下STZ事件总是剪切主控的, 伴随的体胀变形十分微弱(一般比剪切变形小2~3个量级)^[50,51], 因此很难引起显著的体积变化, 更不用说纳米尺度的孔

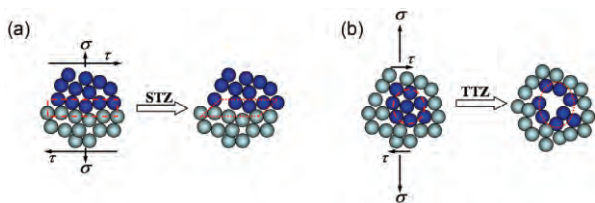


图6 (网络版彩色)非晶合金原子集团运动的剪切转变区(a)^[30]和拉伸转变区(b)^[24]模式

Figure 6 (Color online) Two-dimensional schematics of the atomic group in amorphous alloys, including shear transformation zone (STZ) (a)^[30] and tension transformation zone (TTZ) (b)^[24] modes

洞成核. 尽管如此, 我们仍然可以拟想一种极端情形, 即原子集团的运动不再是剪切主控, 而由体胀主控, 承受显著的静水拉应力. 这种由静水拉应力驱动的局部原子集团运动事件(图6(b)), 被定义为“拉伸转变区(tension transformation zone, TTZ)”^[24]. 概念上, TTZ可以理解成STZ的对立情形, 即原子集团运动由体胀变形为主, 而伴随着微弱的剪切变形^[45]. 一系列的TTZ事件将导致准脆性的纳米尺度孔洞化, 此过程中能量耗散主要是新表面形成. 从原子运动角度看, 纳米周期条痕的形成可以理解为裂尖原子集团以TTZ和STZ模式的交替激活, 其中TTZ诱导的纳米尺度孔洞化是主导过程. 基于这一机制, Jiang等人^[24]预测了纳米周期条痕的特征间距:

$$L = b \left(\frac{\sigma_{th}}{\sigma_y} \right)^2, \quad (1)$$

式中, b 是TTZ的间距($<10 \text{ nm}$)^[52,53], σ_{th} 是拉伸理论强度, σ_y 是拉伸屈服强度. 大量非晶合金数据显示^[24,54,55], $\sigma_{th}/\sigma_y \approx 3$. 因此, 条痕间距预测值 $L < 100 \text{ nm}$, 与实验测量值具有很好的一致性^[24,53]. 通过将裂纹前端纳米尺度孔洞成核与自由体积聚集机制关联, Meng等人^[43]建立了非晶合金动态I型裂纹扩展的理论模型, 预测了裂纹扩展速度随着断裂面形貌从精细涟漪、纳米周期条痕到失稳分叉的演化.

STZ模式的局部原子集团运动本质上一种剪应力驱动下的热激活事件, 且优先在高自由体积区域发生^[30,56-58]. 可以推测, 局部应力状态、温度以及材料微结构都将影响STZ的激活. 因此, 作为STZ的对立模式, TTZ的激活可能需要满足以下两个必要条件: (1) STZ没有足够的时间激活而被抑制; (2) 局部静水拉应力水平达到孔洞成核的临界应力.

因此, 裂纹的动态扩展、裂尖曲率半径减小导致

的应力集中、显著的剪胀效应、低温环境、自由体积减少等条件都将有利于TTZ模式的原子集团运动的激活. 例如, 大量实验都显示^[24,26,36,40,43,59], 纳米周期条痕总是倾向于在I型动态断裂中出现. 原因来自3个方面: 第一, 动态I型裂纹的裂尖曲率半径通常小于裂尖发生流体弯月失稳的临界波长, 从而抑制裂尖塑性在更大尺度(通常在微米尺度)的弯月失稳; 第二, 裂纹动态扩展的时间尺度很短, 导致裂尖塑性的STZ模式没有足够的时间被激活; 第三, 小的裂尖曲率半径使裂尖出现显著的应力集中, 从而可能达到TTZ的临界激活应力. 此外, 纳米周期条痕总是易于在脆性非晶合金体系中出现^[36-38,40,53]. 这一方面是由于脆性体系中自由体积含量相对较低, 导致STZ模式激活困难; 另一方面脆性体系通常拥有更为显著的剪胀效应, 从而有利于原子集团的体胀变形(TTZ). 最近的实验还证实^[26,60], 在足够低的温度条件下, 原子集团更倾向于体胀主控的TTZ模式, 而不是剪切主控的STZ模式.

2.2 分子动力学原子图像

受时空分辨率的限制, 在实验中捕捉这种原子集团体胀变形的TTZ模式十分困难. 分子动力学模拟则提供了这种可能性. 事实上, Falk^[61]在分子动力学(molecular dynamics, MD)模拟中通过压缩原子间相互作用的Lennard-Jones势, 使非晶合金表现出两种截然不同的断裂行为(图7): 一种是脆性断裂, 即裂纹尖端保持原子尺度的尖锐, 并以I型模式向前扩展; 另一种是韧性断裂, 即裂纹尖端由于剪切带激活而显著钝化. 他发现, 对于前一种脆性情形, 断裂能的70%以上耗散于形成新表面, 而后一种情形仅为46%. 此外, 脆性I型裂纹的扩展速度达到了剪切波速的30%左右. 这个数值与Meng等人^[43]理论预测的

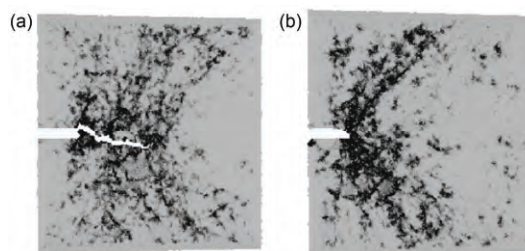


图7 非晶合金脆性(a)和韧性断裂(b)的分子动力学模拟^[61]

Figure 7 MD simulations on the brittle (a) and ductile fracture (b) of an amorphous alloy^[61]

出现纳米周期条痕时I型动态裂纹扩展速度非常接近。尽管Falk当时并未给出脆性I型裂纹扩展的精细过程,但是基于上述结果,可以推测背后的机制可能就是裂尖原子集团的TTZ事件。

美国布朗大学高华健教授及其合作者^[62]通过大规模分子动力学模拟,研究了两种非晶合金样品的单边缺口断裂行为,其中一种是典型的脆性 $\text{Fe}_{80}\text{P}_{20}$ 体系,另一种是典型的韧性 $\text{Cu}_{50}\text{Zr}_{50}$ 体系。模拟结果显示(图8),在相同条件下,韧性体系中缺口裂纹表现出剪切带诱导的尖端钝化行为,而脆性体系的缺口裂纹则以I型模式向前扩展,并且裂尖保持原子尺度的尖锐。这完全重现了Falk关于非晶合金韧脆断裂的模拟结果^[61]。更为重要的是,他们发现脆性体系中I型裂纹是通过裂尖一系列纳米尺度孔洞的成核和连接而向前扩展的,而这些成核的孔洞几乎没有塑性长大过程。很明显,这种成核(新表面形成)主控的纳米尺度孔洞化无法用剪切变形为主的STZ模型描述,而完全符合体胀变形为主的TTZ模型。换句话说,裂尖纳米尺度的孔洞成核本质上源于一系列局部原子集团的TTZ体胀事件(图8(b)),而非STZ剪切事件。这是TTZ模型的原子图像首次在分子动力学模拟被捕捉到。

2.3 TTZ和孔洞化

根据经典理论^[63],孔洞化通常包含成核和长大

两个过程。对于传统晶态金属材料,孔洞化一般发生在微米尺度以上,因此,外部施加的能量绝大部分都耗散于孔洞成核后的塑性长大^[64,65]。但是,非晶合金中孔洞化往往局限在纳米或亚微米尺度,这导致用于孔洞成核的能量耗散(新表面形成)将变得不可忽视,在某些情形下甚至可能超过成核后的塑性长大耗散。非晶合金的脆性断裂就是源于裂尖成核主控的纳米尺度孔洞化,其微观机制是原子尺度密度涨落导致局部应力很容易超过孔洞化临界应力^[62],从而不断激活局部原子集团的TTZ体胀运动。成核主控的孔洞化在宏观上表现为临界静水拉应力对初始的孔洞体积分数不敏感^[62,66]。事实上,在韧性非晶合金体系中,孔洞化仍然由塑性长大主控^[62,67],遵循经典的孔洞化理论。但是,由于孔洞化尺度局限在纳米或亚微米尺度,必须在孔洞成核中考虑托尔曼长度对表面能的影响^[67,68]。孔洞长大由于是塑性流动主控,因此,其微观机制仍然是局部原子集团的STZ剪切运动^[69]。在长时间尺度上,STZ激活引起的结构弛豫将反过来影响孔洞化过程(成核和长大)^[67]。最近,Huang等人^[70,71]系统地研究了非晶合金在拉应力波作用下的层裂行为,证实非晶层裂的微观机制是孔洞化,并观察到层裂随着应变率提高发生韧脆转变现象。基于分子动力学模拟,他们揭示出脆性和韧性层裂分别由孔洞的成核和塑性长大主控,并捕捉到了孔洞成核和长大分别对应的局部原子集团运动,

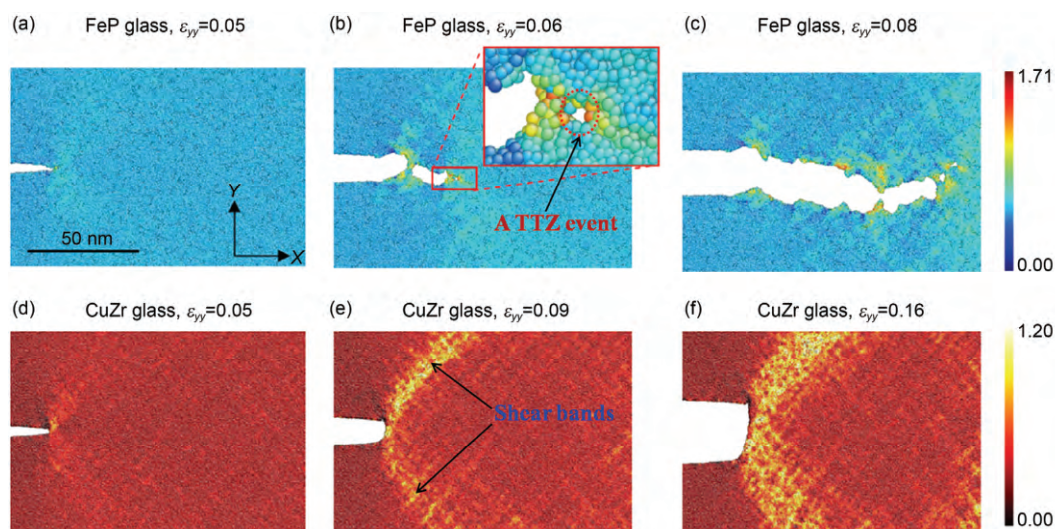


图8 (网络版彩色)非晶合金中裂纹扩展的分子动力学模拟^[62]。(a)~(c) 脆性 $\text{Fe}_{80}\text{P}_{20}$ 体系;(d)~(f) 韧性 $\text{Cu}_{50}\text{Zr}_{50}$ 体系

Figure 8 (Color online) MD simulations on the cracking in amorphous alloys^[62]。(a)~(c) A brittle $\text{Fe}_{80}\text{P}_{20}$ system; (d)~(f) a ductile $\text{Cu}_{50}\text{Zr}_{50}$ system

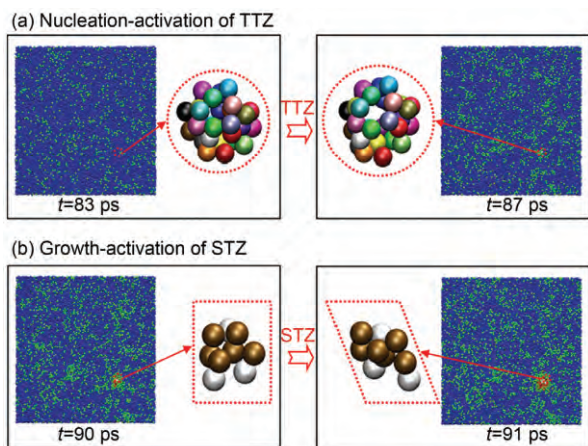


图9 (网络版彩色)分子动力学模拟非晶合金韧性层裂过程中空洞成核(a)和长大(b)分别对应的原子集团TTZ和STZ运动^[71]

Figure 9 (Color online) MD simulations on the nucleation and growth of a void during the ductile spallation of an amorphous alloy, respectively, corresponding to the (a) TTZ and (b) STZ motions of atomic groups^[71]

即TTZ和STZ(图9)。因此, TTZ可以理解为空洞成核或脆性空洞化的基本过程, 而STZ则是空洞塑性长大或塑性空洞化的基本过程。最后还需强调, 经典空洞化所需的静水拉应力一般是直接施加的, 而TTZ激活所需的静水拉应力条件除了直接施加外^[62,71], 还可在剪切模式下通过固有的剪胀效应诱导实现^[26,47]。

3 韧脆转变机理

基于STZ和TTZ模型, 非晶合金在断裂过程中的能量耗散取决于裂尖原子集团到底以STZ还是TTZ模式激活。如果STZ被激活, 局部化塑性流动(剪切带)将诱导裂纹扩展, 使钝化的裂纹面发生流体弯月失稳, 最终在断裂面上形成微米尺度的脉状纹理形貌。如果TTZ被激活, 纳米尺度的空洞化将诱导裂纹以I型模式扩展; 根据成核和塑性长大对能量耗散的相对贡献, 断裂面将呈现百纳米尺度的精细涟漪结构, 甚至纳米尺度的周期条痕结构。由于无序原子系统存在固有的剪胀效应^[46,47], 可以猜测原子集团运动的剪切主控模式(STZ)和体胀主控模式(TTZ)之间是可以逐步过渡, 并在某一临界点可发生模式转变。非晶合金韧脆转变(ductile-to-brittle transition, DBT)在微观上则可以理解为裂尖原子集团运动从STZ向TTZ的临界转变^[24,44,45]。

为了得到非晶韧脆转变的临界条件, Jiang等人^[59]从非晶塑性屈服的协同剪切模型^[54]出发, 理论

推导了STZ的特征体积:

$$\Omega = \frac{k_B T}{4R\zeta G_T \gamma_{CT}^2 (1 - 2G_T \gamma_{CT} / \pi G_0 \gamma_{C0})^{3/2}} \left(\ln \frac{\omega_0}{C\dot{\gamma}} - \frac{1}{\xi} \right), \quad (2)$$

式中, k_B 是玻尔兹曼常数, T 是环境温度, R 是重叠率, ζ 是弹性基体对STZ的约束因子, G_0 和 G_T 分别是绝对零度和环境温度时的剪切模量, γ_{C0} 和 γ_{CT} 分别是绝对零度和环境温度时屈服应变, ω_0 是试探频率, C 是在1量级的无量纲常数, $\dot{\gamma}$ 是外部施加的应变率, ξ 是自由体积浓度。他们认为, STZ的特征体积 Ω 是一个表征临界转变的重要控制参量。当STZ特征体积小于某一临界值 Ω_{cr} 时, 原子集团的STZ运动将被抑制, 而TTZ将被激活, 对应于宏观韧脆转变的发生。可以看出, 式(2)统一了影响非晶合金韧脆转变的外部因素(温度和应变率)和内部因素(自由体积)。针对典型锆基非晶合金开展三点弯、单轴拉伸和单轴压缩实验^[59,60,72], 的确证实降低温度、提高应变率或通过退火消除材料内部自由体积可导致韧脆转变的发生(图10), 即宏观断裂模式从剪切带诱导的剪切断裂转变为拉伸正断, 微观断裂面形貌从微米尺度脉状纹理转变为精细涟漪结构或纳米尺度周期条痕。根据实验结果, 可估算STZ特征体积临界值 $\Omega_{cr} \approx 0.17 \text{ nm}^3$, 意味着此时仅有约9个原子参与STZ事件^[73]。最近, Li等人^[72]基于临界条件 $\Omega = \Omega_{cr}$ 构建了非晶合金韧脆转变与自由体积、温度和应变率的关系图谱, 见图11。

在此基础上, Jiang等人^[51]进一步提出了STZ体胀应变 ϑ 的概念, 将其定义为STZ激活自由体积 v_f^a 与STZ体积 Ω 之比, 即

$$\vartheta = \frac{v_f^a}{\Omega}, \quad (3)$$

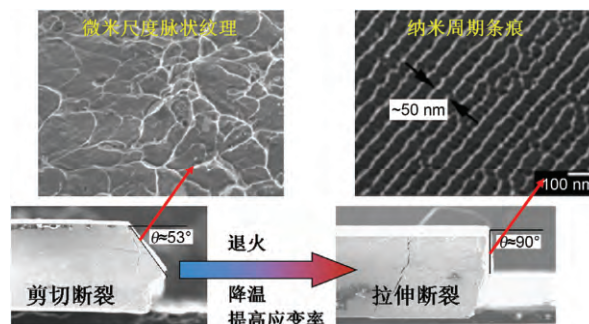


图10 (网络版彩色)影响非晶合金韧脆转变的3个重要因素: 自由体积、温度和应变率

Figure 10 (Color online) Three factors influencing the ductile-to-brittle transition of amorphous alloys: free volume, temperature and strain rates

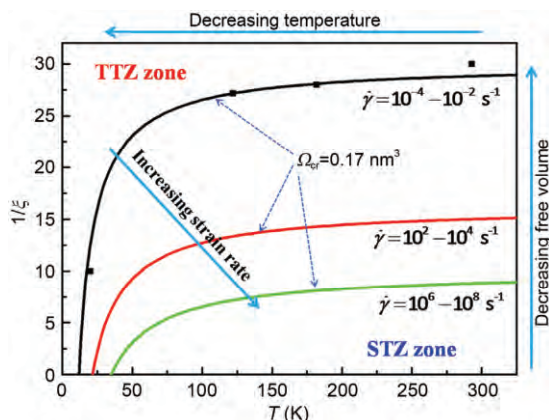


图 11 (网络版彩色)非晶合金韧脆转变与自由体积、温度和应变率的统一关系图谱^[72]

Figure 11 (Color online) The united map showing the relationship between the ductile-to-brittle transition and free volume, temperature and strain rates in amorphous alloys^[72]

式中, v_f^a 理解为在STZ作用下材料内部的可移动自由体积²⁾。以一种典型铅基非晶合金(Vitreloy 1)为模型材料,他们计算了 ρ 随着温度降低的演化。计算结果显示(图12),在室温以下的较大范围内,STZ体胀应变几乎保持不变,仅为其特征剪切应变(0.1)的0.1%左右;但是,随着温度降低至大约15 K时,STZ体胀应变突然急剧增大,远远超过了其特征剪切应变。这意味着,此时原子集团的STZ剪切运动,瞬时转变为体胀主控的TTZ运动。理论预测的临界转变温度非常接近实验上确定的韧脆转变点(大约20 K)^[26]。图12显示,在临界转变温度以上,断裂强度与温度的关系符合Johnson-Samwer $T^{2/3}$ 律^[54]。当温度低于临界转变温度,断裂强度小于Johnson-Samwer $T^{2/3}$ 律的预测,且表现出显著的离散性。这意味着,随着温度降低,原子集团的STZ运动变得越来越困难,激活应力逐渐提高。另一方面,由于固有的剪胀或者剪稀本质,STZ激活应力的提高反过来将增强STZ本身的剪胀能力。当温度降至某一临界温度,STZ的体胀运动(即TTZ)被激活,而剪切运动被彻底抑制,宏观上对应韧脆转变的发生。

4 结语

自1979年Argon^[30]提出STZ模型,到1998年Falk

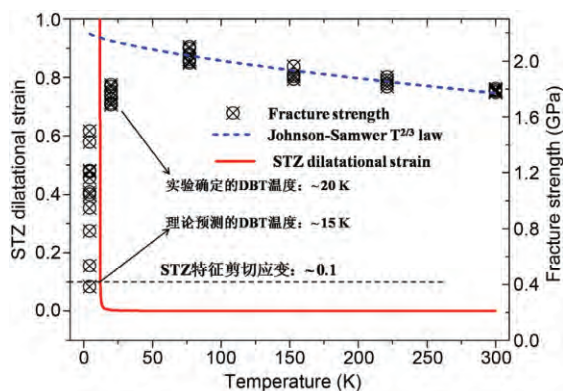


图 12 (网络版彩色)STZ体胀应变^[51]与单轴拉伸断裂强度^[26]随着温度降低的演化

Figure 12 (Color online) STZ dilatational strain^[51] and fracture strength^[26] as a function of temperature

和Langer^[57]在分子动力学模拟中捕捉到,并建立非晶塑性的STZ理论,经历了将近20年时间。之后,STZ的数值模拟和理论分析方面取得了一系列进展^[58,74-78]。尽管如此,由于受时空分辨率的限制以及非晶长程无序的存在,STZ的直接实验验证仍然面临极大的挑战^[79]。从广义上讲,STZ模型描述了偏应力主控下非晶合金中原子集团运动的基本模式,即剪切变形;我们在2008年提出的TTZ模型^[24],描述了静水拉应力主控作用下非晶合金中原子集团运动的基本模式:体胀变形。TTZ模型的提出,完善了非晶合金中原子集团运动的物理图像,使剪切变形和体胀变形有了各自的微观描述。在STZ和TTZ统一框架下,非晶合金的动态断裂^[43,80]、韧脆转变^[26,51,72]、泊松比准则^[81,82]、压力敏感性^[49]和拉压不对称性^[25]等现象都有了相对清晰的物理机制。和STZ一样,TTZ作为原子集团运动的动态事件也面临直接实验验证这一挑战。此外,如何从纳米/亚纳米尺度脆性孔洞化角度,对TTZ进行理论建模需要借鉴经典孔洞化的相关理论成果以及考虑非晶合金独特的结构特征(比如纳米尺度非均匀性、剪胀效应等)。从而,得到TTZ的临界激活能、激活体积、激活频率(时间)和特征空间尺度等重要信息。最后,TTZ如何在时空尺度上动态演化,并引起宏观力学的响应也需要系统深入的研究。

2) 这一概念区别于随着玻璃态转变完成,材料内部冻结的静态自由体积。

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Summary for “非晶合金‘拉伸转变区’模型”

The “tension transformation zone” model of amorphous alloys

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An amorphous alloy is a glassy solid that is formed through the supercooling of a melt. As the melt cools via the glass transition, its atoms freeze into a long-range disordered structure. Amorphous alloys represent a relatively young class of materials, having been first reported in 1960 when Duwez and co-workers produced Au-Si alloys by developing the rapid-quenching technology. The advent of amorphous alloys, especially the bulk samples with their characteristic size in excess of 1 mm, has aroused much interests in the basic science of glass transition, glass structure, and their intriguing properties. For crystalline metals, their structure can be well described by the period lattices and lattice defects including dislocations, twins, stacking faults, grain boundaries, etc. However, these traditional structural defects are not defined in amorphous alloys. Therefore, this type of atomic-disordered alloys manifest a series of excellent mechanical properties, including extraordinary strength, high hardness, large elastic limit and relatively high fracture toughness, making them attractive candidates for many potential applications as structural materials. At temperatures far below the glass transition temperature, the failure of amorphous alloys is generally induced by 10 nm thick shear banding with the single-dominated or multiple mode. It is well known that the shear banding is an instability mode of plastic flow from homogeneous to localized feature. Although the precise mechanism for amorphous plasticity is not well discovered, it is widely accepted that the shear-banding-mediated plasticity originates from a cascade of inelastic shear rearrangements of local atomic groups, called shear transformation zones (STZs). The STZs are thermally activated events with the transient nature, driven by shear stress and giving rise spatially to Eshelby fields. However, many recent works have shown that the failure of amorphous alloys is not always dominated by the shear banding; instead, a brittle failure will take place with a tension mode. The latter is usually accompanied with a new type of fracture surface morphology: fine dimples and/or nanoscale periodic corrugations. In order to understand such a dissipation process of fracture energy, we proposed the “tension transformation zone (TTZ)” model of amorphous alloys in 2008. The TTZ describes the brittle nucleation-controlled cavitation of local atomic groups that can be activated by shear-induced dilatation or direct hydrostatic tension. Here, we review how the TTZ model was developed, including its inherent nature, activation conditions, atomistic simulations and relevant experiments. The difference and relationship between the proposed TTZ and the classical cavitation are extensively discussed. Therefore, the energy dissipation in fracture of amorphous alloys is determined by two competing elementary processes, via. STZs and TTZs ahead of the crack tip. Based on this STZ vs. TTZ picture, the ductile-to-brittle transition of amorphous alloys can be understood as the change in the nature of transformation zones from shear-dominated STZs to dilatation-dominated TTZs. This review ends with the key aspects that deserve further study regarding the TTZ model. These aspects, at least, include (1) the experimental capture of TTZs, (2) the dynamics properties, (3) the spatio-temporal evolution, and (4) the theoretical construction from TTZs to brittle failure in amorphous alloys.

amorphous alloys, shear band, fracture, shear transformation zone, tension transformation zone

doi: 10.1360/N972016-00509