



非晶合金弛豫子及相互作用研究进展

宋丽建^{*}, 童钰, 许巍, 高萌, 张岩, 霍军涛, 王军强^{*}

中国科学院宁波材料技术与工程研究所, 中国科学院磁性材料与器件重点实验室, 浙江省磁性材料及其应用技术重点实验室, 宁波 315201

^{*}联系人, 宋丽建, E-mail: songlj@nimte.ac.cn; 王军强, E-mail: jqwang@nimte.ac.cn

收稿日期: 2024-09-25; 接受日期: 2024-12-10; 网络出版日期: 2025-03-10

国家自然科学基金(编号: 52231006, 92163108, 52271158)、浙江省自然科学基金(编号: LGF22E010002, LZ22A030001, LR22E010004)、浙江省“尖兵”“领雁”研发攻关计划(编号: 2022C01023)和宁波市“科技创新2025”重大专项(编号: 2022Z033)资助项目

摘要 非晶/玻璃等非平衡态材料会自发向低能量状态转变, 称为老化或弛豫, 表现出非指数的演化特征. 人们认为非晶/玻璃的非指数弛豫是由不同的局域弛豫谱叠加而来. 然而, 关于非指数弛豫的起源仍不清晰. 这篇综述简要介绍了非晶合金等温弛豫行为, 探测到符合Debye方程的弛豫基本单元——弛豫子, 且不同弛豫子相互作用会激活记忆效应. “弛豫子”概念的提出为理解非平衡态材料的物理本质、编程式设计等温退火工艺以及精准调控其性能具有重要意义.

关键词 非晶合金, 弛豫子, 记忆效应

PACS: 71.23.Cq, 61.20.Lc, 83.85.St

1 引言

玻璃物质(或非晶态材料)是人类生活中常见的, 也是生产生活中不可或缺的重要材料. 非晶合金作为玻璃物质的新成员, 仅有60多年的发展历史. 其制备工艺主要是利用高温熔体快速冷却, “冻结”熔体原子的无序结构形态. 相比于晶体合金材料, 非晶合金表现出优异的软磁性能、耐腐蚀、高强度和高硬度等特性, 在电力电子、航空航天、催化等领域具有重要应用前景.

非晶合金由于无序的原子结构特征, 致使传统晶体材料基于晶体结构、晶粒尺寸、位错等构建结构-性能的关系存在明显局限性. 从能量角度讲, 非晶合金是一种亚稳材料, 具有丰富的能量状态. 不同能量状态

相互转化的过程中会伴随着复杂的弛豫模式. 按照特征频率, 由慢到快可以分为 α 弛豫、 β 弛豫、 γ/β' 弛豫、玻色峰和双能级弛豫等^[1-4], 如图1所示. 一般认为, α 弛豫是大尺度的原子协同运动, 弛豫频率低; β 弛豫和 γ/β' 弛豫则是更加局域的原子链状运动过程, 弛豫频率高^[5,6].

实验研究表明, 非晶体系在温度和应力等外场作用下的等温弛豫过程均表现出非指数的弛豫特征, 可以通过Kohlrausch-Williams-Watts (KWW)方程进行描述^[7,8]:

$$\phi(t) = A \exp \left[- \left(\frac{t}{\tau} \right)^{\beta_{\text{KWW}}} \right], \quad (1)$$

引用格式: 宋丽建, 童钰, 许巍, 等. 非晶合金弛豫子及相互作用研究进展. 中国科学: 物理学 力学 天文学, 2025, 55: 286103

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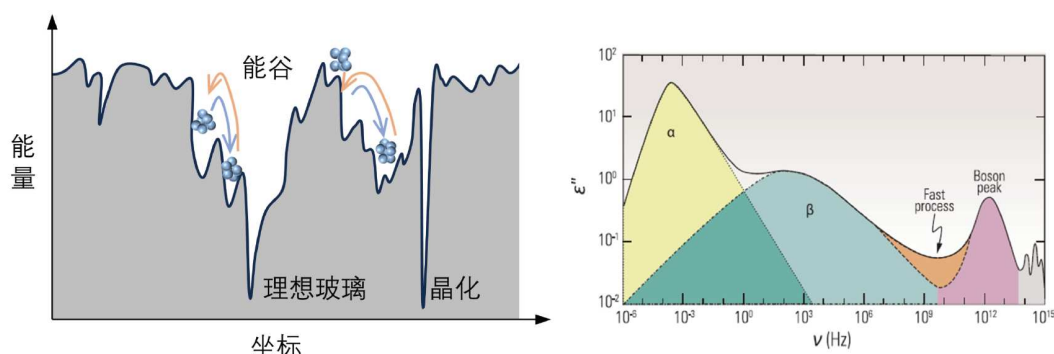


图 1 (网络版彩图)非晶态物质的能量地形图(左)和弛豫谱(右)^[3]

Figure 1 (Color online) Schematic illustration of the potential energy landscape (left) and spectrum of relaxation dynamics (right) of amorphous [3]. Adapted from ref. [3] with permission.

其中, A 是拟合常数, τ 是特征弛豫时间, β_{KWW} 是非指数参量. 宏观非指数的弛豫谱是由一系列的局域特征弛豫谱叠加而来, 如图2所示. 目前, 有关宏观非指数特征的起源存在两种主要假说: 一种是来自具有指数特征的局域弛豫谱的叠加, 即非均匀性假说; 另一种是局域弛豫与宏观弛豫谱具有相同的非指数行为, 即均匀性假说^[9,10]. 早在1995年, 研究人员基于烧蚀(Hole-Burning)技术为弛豫谱可能起源于指数动力学的响应提供了一些实验证据^[11]. 然而, 关于指数型弛豫谱的系统性研究仍缺少直接的实验证据, 研究其物理起源及相互作用关系对理解玻璃本质以及建立结构与性能间关系具有重要意义.

2 非晶合金弛豫基本单元——弛豫子的探测

国内外研究人员围绕非晶态材料非平衡亚稳特征, 利用核磁共振技术、X射线光子相关光谱学、动态力学分析和差示扫描量热技术等研究结构弛豫的演化规律. 例如, Reuhl等人^[12]利用核磁共振技术研究发现, 乙二醇中 ^2H 的磁化强度随时间的演化表现出非指数的演化行为, 可以利用多个KWW方程的叠加进行描述. Evenson等人^[13]利用X射线光子相关光谱学技术揭示非晶合金微观原子的间歇式运动机制, 为非指数弛豫提供了微观视角. 非晶态材料微观结构随时间发生改变时, 宏观上随着时间的增加, 其黏度、应力-应变、能量状态等也表现出非指数行为. Qiao等人^[14]和Zhang等人^[15]发现非晶合金的应力松弛无法采用单一指数方程或Debye方程描述, 并据此揭示出非晶合金

中存在的两种新弛豫模式: 一种是应力驱动主导, 另一种是热激活主导. Luo等人^[16]根据非晶合金应力松弛的非指数特性同样揭示出玻璃态动力学模式的劈裂现象. 此外, Hu等人^[17,18]在非晶合金和氧化物玻璃的焓弛豫过程中也观察到非指数的现象. Yang等人^[19]利用高精度闪速差示扫描量热仪(Flash DSC)测量了不同非晶合金体系玻璃转变随升温速率的依赖性, 与力学弛豫谱的演化规律一致, 意味着玻璃转变具有非指数弛豫行为. Gallino等人^[20]在测量非晶合金焓随时间的演化时, 发现存在分层级的弛豫过程. 从物理本质讲, 不同表征技术均会涉及原子结构的重组, 因而观测非晶合金弛豫的非指数行为具有普遍性.

需要指出的是, 理解非晶合金非指数弛豫是发展精准调控非平衡态进而改善软磁、力学等性能的关键. 基于非晶合金能量状态的可调控特性, 研究人员利用高精度闪速差示扫描量热仪测量了不同退火温度和退火时间下的弛豫热流峰^[21]. 非晶合金在不同退火温度以及不同退火时间下弛豫热流峰, 在半对数曲线下表现出 α 弛豫峰伴随着宽泛的肩膀状 β 弛豫峰(图2). 而且, 这些独立的弛豫热流峰叠加形成的轮廓与动态力学分析仪(DMA)的损耗谱峰具有一致性(图2). 对比非指数的Havriliak-Negami (HN)方程和Debye方程:

HN方程

$$E = E_{\mu} + \frac{E_{\mu} - E_r}{\left[1 + (i\omega\tau)^a\right]^b}, \quad (2)$$

Debye方程

$$E = E_{\mu} + \frac{E_{\mu} - E_r}{1 + i\omega\tau}, \quad (3)$$

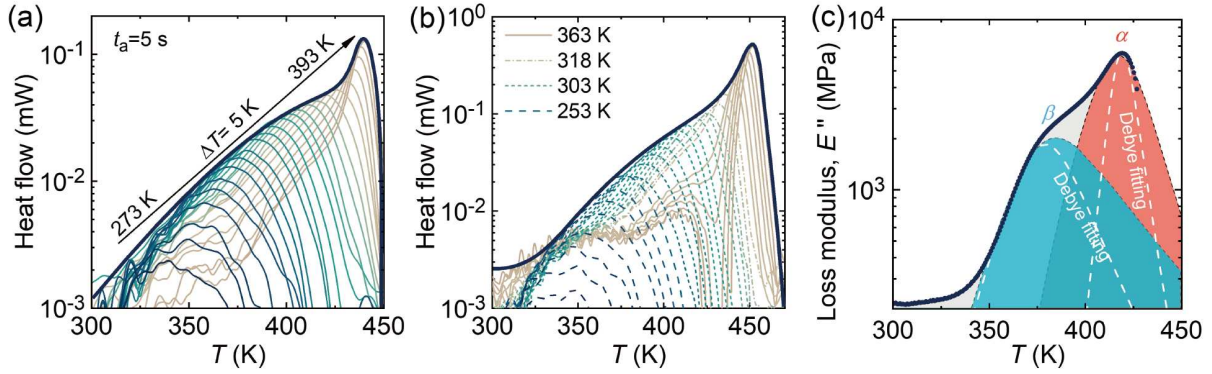


图 2 (网络版彩图) (a) Au基非晶合金在退火温度 $T_a=273\text{--}393\text{ K}$ 下退火 5 s 的热流弛豫峰^[21]. (b) Au基金属玻璃在退火温度 $T_a=253, 303, 318, 363\text{ K}$ 下的热流弛豫峰^[21]. (c) Au基非晶合金的损耗模量-温度谱^[21]

Figure 2 (Color online) (a) Heat flow peaks for Au-based metallic glass being annealed at $T_a = 273$ to 393 K for $t_a = 5\text{ s}$ [21]. (b) Heat flow peaks for Au-based metallic glass being annealed at $T_a = 253, 303, 318, 363\text{ K}$, respectively [21]. (c) Temperature-dependent loss modulus of Au-based metallic glass [21]. Adapted from ref. [21] with permission.

其中, E 是复合模量, E_μ 是非弛豫模量, 表示未发生弛豫时的模量, 也即初始模量, E_r 是弛豫模量, 表示变温或变频过程的即时模量, i 是虚部, ω 是角频率, τ 是特征弛豫时间, a 和 b 是拟合参数, 且拟合范围为 $0\text{--}1$. 当 $a = b = 1$ 时, HN方程转换为Debye弛豫形式. 对于损耗模量, 仅有一个特征弛豫时间或激活能的Debye方程拟合峰宽更窄, 而包含弛豫时间分布的HN方程可以很好地描述整个实验曲线, 意味着非指数谱峰可以分解成独立的子峰.

对于热流弛豫峰, Debye方程可以表示为

$$Q(t) = Q_0 \left[1 - \exp\left(-\frac{t}{\tau(T)}\right) \right] \quad (4)$$

连续升温过程需要考虑升温速率, 式(4)可以改写为

$$Q(t) = Q_0 \left[1 - \exp\left(-\int_{t_s}^t \frac{dt}{\tau(T)}\right) \right] \\ = Q_0 \left[1 - \exp\left(-\int_{T_s}^T \frac{dT}{R_h \tau(T)}\right) \right] \quad (5)$$

其中, Q_0 是拟合常数, $\tau(T)$ 是特征弛豫时间, t_s 是起始时间, T_s 是起始温度, R_h 是升温速率. 一般而言, $\tau(T)$ 存在两种形式: 一种是Arrhenius形式, $\tau = \tau_0 \exp(E^*/RT)$; 另一种是VFT形式, $\tau = \tau_0 \exp[DT_0/(T-T_0)]$. 其中, E^* 是激活能, R 是气体常数, τ_0 是拟合常数, D 是强度参数, T_0 代表拟合温度常数. 不同退火条件下的热流弛豫谱峰可以利用式(5)进行很好的拟合, 得到特定弛豫状态的激活能. 发现激活能在 γ/β' 弛豫和 β 弛豫阶段不断增大, 而

在 α 弛豫阶段趋于稳定.

热流谱峰结果表明, 后续升温会以指数动力学的线性响应方式激活等温退火过程中弛豫事件(图3). 这一结果与Richert等人^[10,22]认为非晶态物质结构不均匀性是由具有不同特征弛豫时间的单元组成相一致. 根据玻璃转变的弹性理论模型, 非晶合金的非平衡弛豫与材料弹性性质相关^[23–25], 意味着指数弛豫事件可能服从玻尔兹曼统计分布. 这些结果为建立非晶态材料非平衡热力学提供了重要的实验证据.

从应用角度讲, 精准独立调控热流弛豫谱对改善非晶合金性能至关重要. 通过对非晶合金进行单步、双步和三步等温退火, 可以分别激活一个、两个和三个热流弛豫谱(图4). 值得注意的是, 低温退火重新激活的弛豫谱峰是在原来谱峰基础上进行局域的激活, 而不需要谱峰的整体响应, 表明指数弛豫谱峰可以进行独立调控和/或组合.

为了分析不同模式的弛豫子在焓空间的演化规律, 进一步构建了激活能随弛豫焓和退火温度的三维轮廓图. 对于高温长时间退火, 激活能近似等于 $350\text{--}460\text{ kJ/mol}$, 与 α 弛豫的激活能相当. 对于中间退火阶段, 激活能约为 $80\text{--}120\text{ kJ/mol}$, 与 β 弛豫相当. 而低温短时间退火, 激活能约为 40 kJ/mol , 符合 γ/β' 弛豫的激活能. 可以看出, 样品在等温退火过程中依次经历了 γ/β' 弛豫、 β 弛豫和 α 弛豫, 并在焓空间中实现了对不同模式弛豫子含量的定量表征(图5). 从 γ/β' 弛豫到 β 弛豫, 再到 α 弛豫的等温退火转变意味着自由体积的湮灭^[26,27]. 样品未经退火处理时, 原子间具有低的堆积

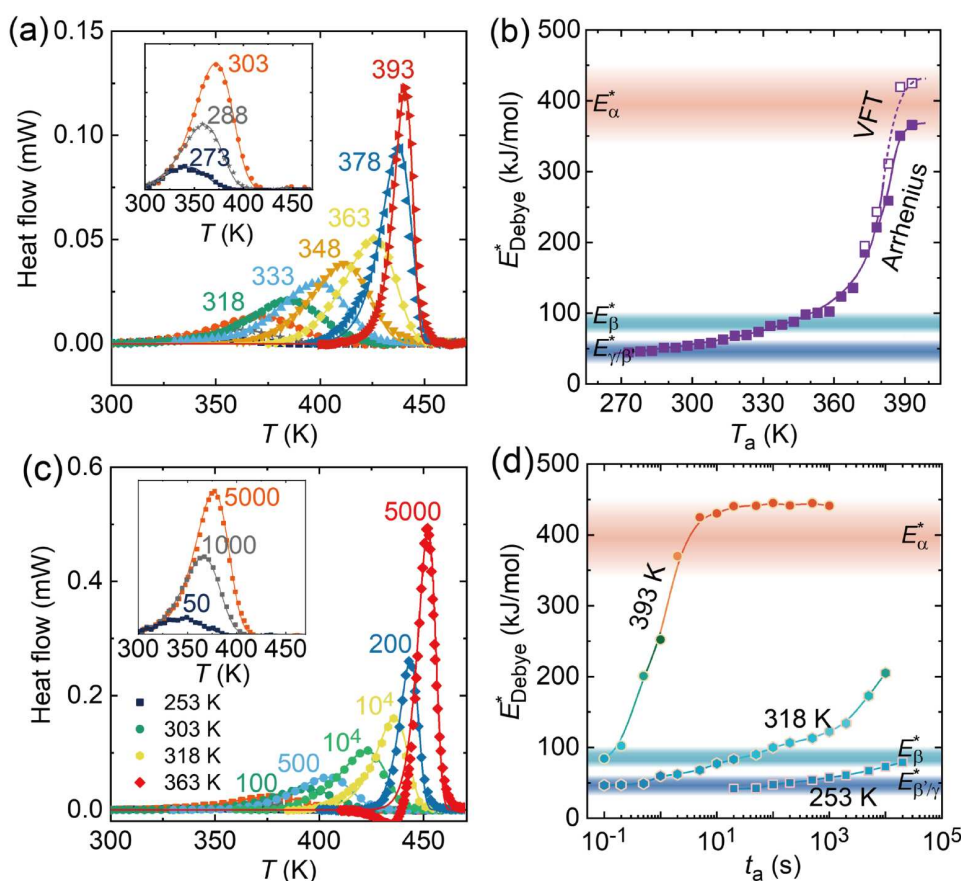


图 3 (网络版彩图) (a) Au基非晶合金在退火温度 $T_a = 273\text{--}393$ K下退火5 s的热流弛豫峰(实点)与Debye模型拟合(实线), 插图为 $T_a = 273, 288, 303$ K的热流弛豫峰图[21]. (b) (a)图中退火条件下的弛豫激活能[21]. (c) Au基非晶合金在退火温度 $T_a = 253, 303, 318, 363$ K下退火不同时间的热流弛豫峰(实点)与Debye模型拟合(实线), 插图为低温短时间退火的热流弛豫峰图[21]. (d) (c)图中退火条件下的弛豫激活能[21]

Figure 3 (Color online) (a) Heat flow data of Au-based amorphous alloy (solid symbols) at $T_a = 273\text{--}393$ K for $t_a = 5$ s fitted using the Debye model (solid curves). Inset is the relaxation peak at $T_a = 273, 288$, and 303 K [21]. (b) Relaxation activation energy under different annealing conditions in (a) [21]. (c) Heat flow data of Au-based metallic glass (solid symbols) at $T_a = 253, 303, 318, 363$ K fitted using the Debye model (solid curves). Inset is the relaxation peak at lower temperature and shorter annealing time [21]. (d) Relaxation activation energy under different annealing conditions in (c). [21]. Adapted from ref. [21] with permission.

密度(如类液体区或者流变单元[6,28,29]), 原子之间的协同性比较弱, 运动更加容易, 对应于快的弛豫过程; 随着退火时间增长, 原子间排列紧密(如类固体区[28,30]), 呈现出更强的协同性, 需要大尺度的协同运动方式, 也就是 α 弛豫模式。

3 弛豫子相互作用激活记忆效应

与单步退火不同, 非晶态材料进行先低温后高温双步退火时焓或体积会先升高再降低至平衡态。这种反常的焓或体积升高引起的“年轻化”现象称为Kovacs记忆效应[31]。研究发现记忆效应在高分子玻璃、氧化

物玻璃、电子玻璃、非晶合金等无序体系中广泛存在[32–38], 与材料的化学键性质没有明显关系。这些非晶态材料的记忆效应有明显的热激活特征, 改变两步退火过程的温度和时间都会对记忆效应的强度和时间产生明显影响, 比如, 增加第一步低温退火时间, 可以显著提高记忆效应的强度[32]。甚至对非晶材料进行“训练”, 将第二步高温退火过程分解成多个中间温度退火, 记忆效应会得到显著增加[37]。除了高温结构弛豫外, 在低温玻色峰中也存在记忆效应, 这一结果证实了玻色峰与结构弛豫的内禀关联性[39]。经典Tool-Narayanawamy-Moynihan (TNM)模型认为记忆效应起源于不均匀性结构, 通过调节两个虚拟温度的比例

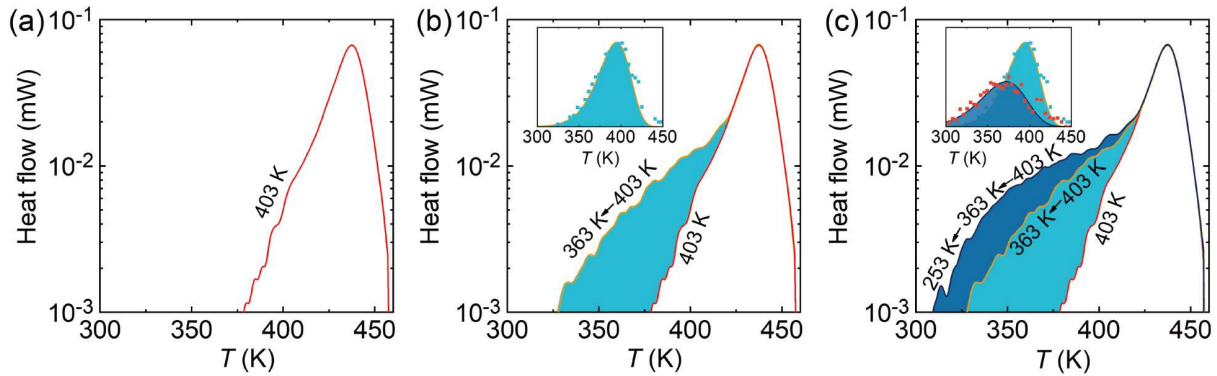


图 4 (网络版彩图) (a) Au基非晶合金在退火温度 $T_a = 403$ K下退火0.5 s的热流弛豫峰^[21]. (b) Au基非晶合金先在 $T_a = 403$ K退火0.5 s, 然后降低至 $T_a = 363$ K退火0.1 s的热流弛豫峰, 插图为两个热流弛豫峰相减获得^[21]. (c) Au基非晶合金先在 $T_a = 403$ K退火0.5 s, 然后降低至 $T_a = 363$ K退火0.1 s, 最后在 $T_a = 253$ K退火500 s的热流弛豫峰, 插图分别为通过减去双步和三步退火样品的热流弛豫峰获得^[21]

Figure 4 (Color online) (a) Heat flow peak for Au-based amorphous alloy being annealed at $T_a = 403$ K for $t_a = 0.5$ s [21]. (b) Heat flow peaks for Au-based amorphous alloy being annealed at $T_a = 403$ K for $t_a = 0.5$ s then at $T_a = 363$ K for $t_a = 0.1$ s. Inset is the relaxation peak by subtracting the two heat flow peaks [21]. (c) Heat flow peaks for Au-based amorphous alloy being annealed successively at $T_a = 403$ K for $t_a = 0.5$ s then $T_a = 363$ K for $t_a = 0.1$ s and finally being annealed at $T_a = 253$ K for $t_a = 500$ s. Inset is the relaxation peak obtained by subtracting the heat flow peaks of two-step and three-step annealing samples, respectively [21]. Adapted from ref. [21] with permission.

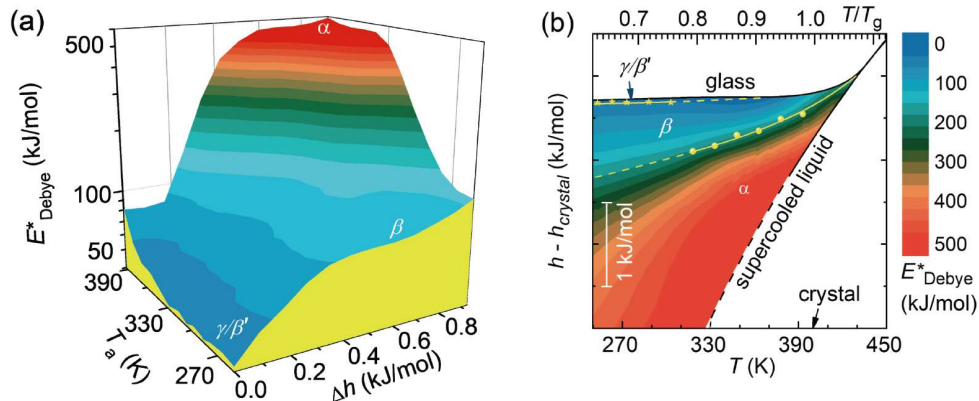


图 5 (网络版彩图) (a) 激活能 E_{Debye}^* 与退火温度和弛豫焓变的关系^[21]. (b) 不同弛豫模式演化的温度-焓变相变^[21]

Figure 5 (Color online) (a) Dependence of activation energy E_{Debye}^* on the enthalpy change of samples annealed at a wide temperature range [21]. (b) Temperature-enthalpy change diagram of different relaxation modes [21]. Adapted from ref. [21] with permission.

可以定性地拟合非晶的记忆效应^[40–42]. 此外, 褶皱纸张、摩擦表面、颗粒材料等很多非热激活无序体系, 在外加应力或电场的驱动下, 也都呈现出类似的记忆效应^[43–48]. 现有研究表明, 无序体系具有记忆效应是普适的, 不受化学成分、化学键以及相互作用形式等的影响.

事实上, 非晶合金的焓记忆效应在不同退火温度间转变时涉及不同弛豫动力学的错配^[32,36,49]. 例如, 预退火时间非常短时不会出现记忆效应, 只有预退火时间足够长时才可以激活记忆效应^[35]; 而且低温玻色峰

中也存在记忆效应^[36]. 对于相同的预退火时间, 焓回复到最大值所需时间随预退火温度的升高而增加(图6). 此外, 对非晶合金退火过程进行“训练”, 将第二步高温退火过程分解成多个中间温度退火, 记忆效应会得到显著增加^[37]. 这些结果说明记忆效应不仅依赖于预退火的温度, 还依赖预退火时间.

熵作为一个重要的物理量, 表达了能量变化和时间方向的普适性. 多位著名非晶态物理学家在*Review of Modern Physics*期刊发表综述文章, 指出熵可能在记忆效应中具有重要作用^[50]. Cagle Jr.和Eyring^[51]引入

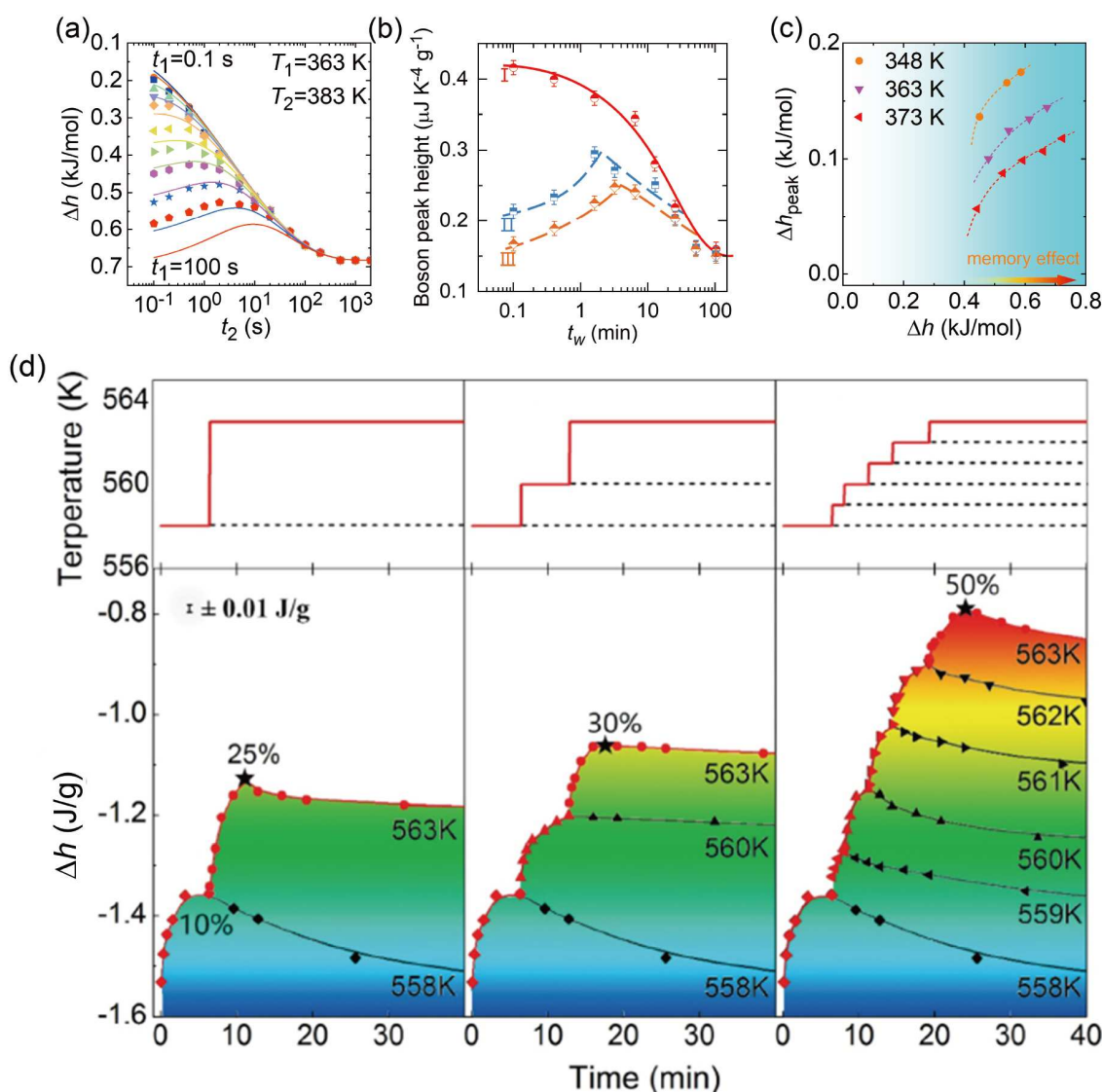


图 6 (网络版彩图) (a) $T_2 = 383$ K 下样品的焓随时间的演化关系, 预退火条件: $T_1 = 363$ K, $t_1 = 0.1\text{--}100$ s^[35]. (b) 单步(曲线 I)和双步(曲线 II 和曲线 III)等温退火过程中玻色峰强度^[36]. (c) 记忆效应强度与预退火焓变关系^[35], 虚线为引导线. (d) 利用多步退火温度和时间“训练”记忆效应^[37]

Figure 6 (Color online) (a) The enthalpy change following annealing at $T_2 = 383$ K for the sample pre-annealed at $T_1 = 363$ K for $t_1 = 0.1\text{--}100$ s^[35]. (b) Boson peak height for single (curve I) and two-step (curve II and curve III) isothermal annealing^[36]. (c) The strength of memory effect (Δh_{peak}) versus enthalpy evolution (Δh)^[35]. The dashed lines are for guides for the eyes. (d) Memory effect of multistep training by multi-step annealing temperature and time^[37]. Adapted from refs. [35–37] with permission.

过渡态理论(或绝对反应速率理论)来理解晶体和非晶态材料的退火弛豫过程, 获得了弛豫过程的激活焓和激活熵特征. 利用过渡态理论分析不同弛豫子的激活焓和激活熵时, 发现激活焓 S^* 变化更为剧烈, 而且高温退火阶段跳转到具有大激活焓的非晶态时才出现记忆效应, 表明熵在记忆效应中具有关键作用(图7). 换句话说, 当从具有小激活焓的 β 弛豫子跳入具有大激活

焓的 α 弛豫子区间时, 相同焓变的获取路径方式不同, 存在低温预退火演化的最优结构路径与高温阶段错配, 第二步高温退火需要通过增加焓变来打破原来的演化路径, 激活记忆效应(图7). 最近的理论工作通过对不同时间下的微观尺度模拟, 探讨了激活焓在非晶态物质全局与局部变形中所起的作用, 揭示出 β 弛豫的强焓变效应, 并从非晶态材料角度验证了焓-熵补偿

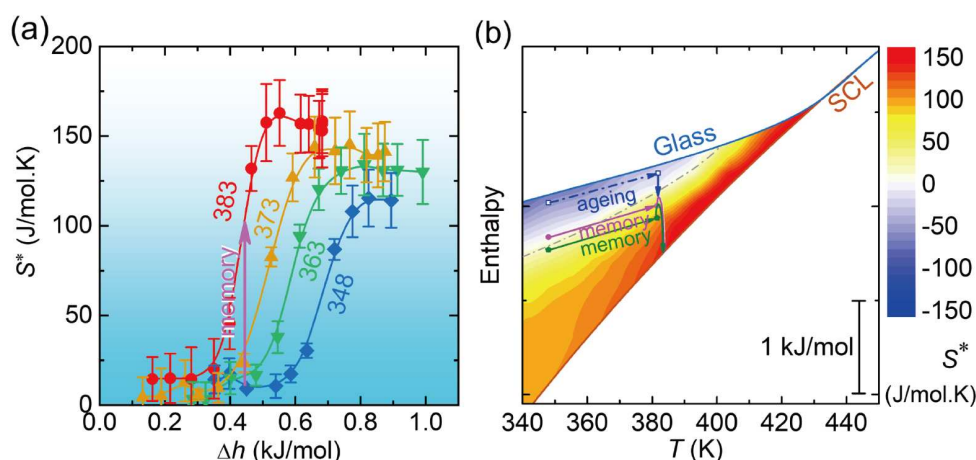


图 7 (网络版彩图) (a) 不同退火条件下弛豫熵与激活熵的演化关系^[35]. (b) 等温退火过程的焓变示意图. 蓝色空心正方形表示 $T = 348$ K 预退火 $t_a = 1$ s; 粉色圆点表示 $T = 348$ K 预退火 $t_a = 20$ s; 绿色五边形表示 $T = 348$ K 预退火 $t_a = 100$ s^[35]

Figure 7 (Color online) (a) Activation entropy as a function of enthalpy change at different annealing conditions [35]. (b) Schematic map of enthalpy changes during isothermal annealing. Open blue squares: the sample pre-annealed at $T = 348$ K for 1 s. Filled pink circles: the sample pre-annealed at $T = 348$ K for 20 s. Filled green pentagons: the sample pre-annealed at $T = 348$ K for 100 s [35]. Adapted from ref. [35] with permission.

效应^[52–54]. 不同弛豫状态的熵效应反映了激活途径的多样性, 为实验结果提供了更充分的理论证据.

非晶合金作为结构材料应用时, 存在应力松弛/弛豫现象, 会削弱材料的承载能力和稳定性. 例如, 在恒定应变速率下, 非晶合金会发生均匀形变过程^[55–58]. Tong 等人^[57]在焓记忆效应基础上, 通过对非晶合金先加载高应变后加载低应变实现了应力先升高后降低的应力记忆效应(图8), 显著降低了形变发生过程. 原位拉伸高能同步辐射实验显示, 非晶合金在应力松弛过程中, 原子堆积密度随着应变增大而增大, 主要是由于小原子在大溶剂原子形成的网络内的扩散所导致的; 而应力记忆效应阶段则源于小原子向更疏松的原子堆积结构的扩散, 揭示应力记忆效应是由可逆 β 弛豫子主导的物理图像(图8). 第二阶段恒应变加载时出现的反常应力递增现象, 可以显著抵抗因应力衰减导致的结构失效, 为研究非晶态材料抵抗应力松弛能力提供了新途径.

非晶合金经历等温退火一般会变脆, 而通过焓记忆效应可以极大改善其塑性形变能力. Ketov 等人^[59]利用冷热循环处理提升非晶合金的能量, 激活更多的流变单元, 显著提升压缩塑性. Meng 等人^[60]发现焓记忆效应会增加原子疏松堆积区比例, 使得“回春”后的非晶合金塑性和断裂韧性优于淬态样品. 对于软磁性而言, 非晶合金的黏弹性/结构不均匀性不利于提升

软磁性能^[61], 但焓记忆效应却实现了软磁性能与力学性能的双重改善^[62]. Zheng 等人^[63]发现冷热循环处理改善了退火后非晶合金的弯曲塑性, 且能够保持软磁性能基本不变, 而随着冷热循环处理次数的增加, 铁基非晶合金的软磁性能会出现波动^[64]. 从空间科学角度, 经历亿万年以上弛豫的月壤非晶态材料是研究弛豫动力学、超稳特性等的一种理想模型体系. Li 等人^[65]在研究嫦娥五号月壤存储氢-3时, 发现太阳风辐照会诱导钛铁矿表面形成非晶层, 并在非晶层中发现了大量的氦气泡, 而钛铁矿颗粒内部晶体中, 基本没有氦气泡. 说明钛铁矿非晶层稳定性极高, 且具有更加致密的原子排列结构, 避免了沟道效应, 可以将太阳风中的氦捕获并存储起来, 形成了以气泡形式存储的氢-3资源.

4 总结与展望

非晶合金的非平衡亚稳特性蕴含着丰富的物理响应机制, 能量状态和弛豫作为其本征属性, 不同能量状态间的转化、弛豫模式间的相互作用以及它们与物理化学性能间的关系认识仍不够明晰. 本文从非晶合金能量和弛豫动力学角度, 简述了符合Debye指数方程的弛豫基本单元——弛豫子的探测以及相互作用的研究进展, 但有关弛豫子的研究还存在很多问题有待深

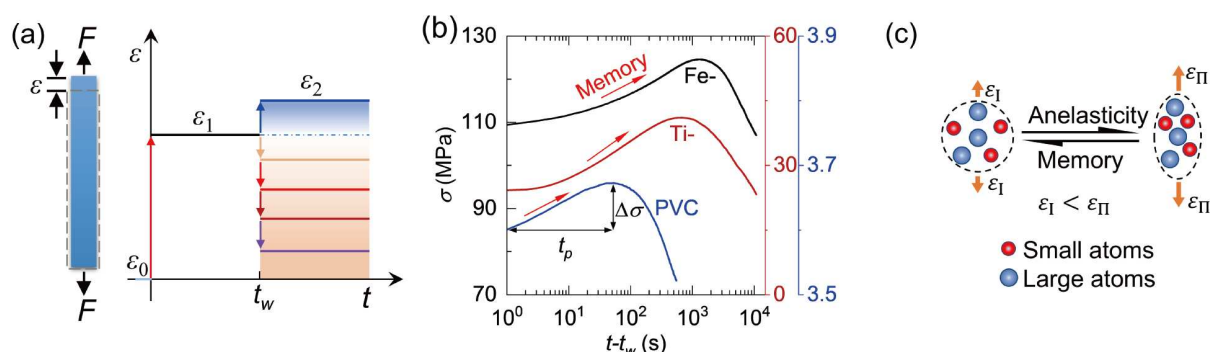


图 8 (网络版彩图) (a) 双步应变加载示意图^[57]. (b) 在铁基、钛基非晶合金以及PVC体系中存在应力记忆效应^[57]. (c) 原子堆积结构在滞弹性应力弛豫和记忆回复过程中的演化示意图, 记忆效应与可逆的 β 弛豫存在内禀关联^[57]

Figure 8 (Color online) (a) Two-step strain annealing protocol [57]. (b) The semi-logarithmic plots of non-monotonic stress relaxation curves for three glasses (Fe-based amorphous alloy, Ti-based amorphous alloy, and PVC) [57]. (c) The schematic illustration for the evolution of atomic packing structure for anelastic stress relaxation and recovery memory process. Intrinsic correlation stress memory effect and reversible β relaxations [57]. Adapted from ref. [57] with permission.

入探索. 一方面, 非晶合金在不同外场(如温度场、应力场、电场、磁场等)激励下弛豫子的响应行为, 定量调控弛豫子的峰宽、峰位和峰高等谱峰信息; 另一方面, 非晶合金中不同弛豫子间的相互作用, 探索多弛

豫子共存解决不同性能间的协同强化问题, 如铁基非晶合金力学塑性与软磁性能二者不可兼得的矛盾. 希望基于弛豫子的探测可以为非晶合金研究提供一些借鉴.

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Relaxun and their interaction in amorphous alloys

SONG LiJian^{*}, TONG Yu, XU Wei, GAO Meng, ZHANG Yan,
HUO JunTao & WANG Jun-Qiang^{*}

CAS Key Laboratory of Magnetic Materials and Devices, and Zhejiang Province Key Laboratory of Magnetic Materials and Application Technology, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

**Corresponding authors (SONG LiJian, email: songlj@nimte.ac.cn; WANG Jun-Qiang, email: jqwang@nimte.ac.cn)*

Amorphous or glassy systems will relax toward a low energy state, namely “aging or relaxation”, which exhibits a non-exponential character. Generally, the non-exponential relaxation peaks are composed of a series of local relaxation events. However, the physical description of non-exponential relaxation is still not clear. This article introduces the isothermal annealing behaviors of amorphous alloys. The relaxation units (relaxun), which obey the Debye equation, were detected, and the interaction of different relaxuns can activate the memory effect. The concept “relaxun” is of great significance for understanding the physical nature of non-equilibrium materials, controlling isothermal annealing processes and precisely modulating the properties of amorphous materials.

amorphous alloys, relaxun, memory effect

PACS: 71.23.Cq, 61.20.Lc, 83.85.St

doi: [10.1360/SSPMA-2024-0409](https://doi.org/10.1360/SSPMA-2024-0409)