

Ni-Cr 合金真空钎焊金刚石的表面石墨化

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摘 要: 以 Ni-Cr 合金为钎料采用真空钎焊的方法制备了金刚石钎焊试样. 运用扫描电镜(SEM)、X 射线能谱仪(EDS)及显微激光拉曼光谱仪对钎焊金刚石表面石墨化的形貌、石墨化程度进行了综合分析. 结果表明, 在 Ni-Cr 合金钎料真空钎焊金刚石的过程中, 金刚石的表面生成了石墨, 其厚度约为 $10\mu\text{m}$; 而钎焊过程中, 金刚石表面 C 原子结构的破坏、解体以及降温过程中 C 原子的析出和再结晶是导致金刚石石墨化的原因; 钎焊时在金刚石表面先生成石墨后生成碳化物.

关键词: 镍基合金; 真空钎焊; 金刚石; 石墨化

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0 序 言

由于在钎焊工艺过程中, 金刚石和钎料之间实现了化学冶金结合以及钎料对金刚石的浸润和爬升, 钎焊金刚石工具解决了传统金刚石工具上金刚石把持力不够和金刚石磨粒出露高度过低的问题^[1,2]. 故自上世纪 90 年代以来, 国内外便掀起了研究单层钎焊金刚石工具的高潮, 在钎焊机理和钎焊工艺等方面都进行了较为深入的研究^[3,4].

目前, 许多文献对 Ni-Cr 合金钎料真空钎焊金刚石的机理、界面反应生成物的形貌、结构进行了研究, 认为在钎焊过程中 Ni-Cr 合金中钎料会在金刚石界面形成富铬层并与金刚石表面的 C 元素反应生成笋状的 Cr_7C_3 和片状的 Cr_3C_2 , 是实现合金层与金刚石有较高结合强度的主要因素^[3]. 但是其钎焊机理的研究并不完善, 因为钎焊是在高温下进行, 而且 Ni-Cr 合金中的 Ni 元素在高温下使金刚石表面发生石墨化^[5], 且金刚石与金属铁、钴、镍共存时约 $700\text{ }^\circ\text{C}$ 开始石墨化^[6], 故钎焊时处于亚稳结构的金刚石有可能产生石墨化, 而目前对于金刚石表面的石墨化却缺乏深入的研究.

通过对 Ni-Cr 合金钎料真空钎焊金刚石的表面石墨化的形貌观察, 着重分析了金刚石表面石墨形貌、石墨化程度以及碳化物的形成, 以期对钎焊金

石的机理研究做一些有益探索.

1 试验方法

试验选用 YK-9 金刚石, 粒度为 40/50 ($300\sim 425\mu\text{m}$), 钎料为 Ni-Cr 合金, 基体为 45 钢. 钎焊前对 45 钢基体、金刚石表面去油去污处理. 金刚石直接排布在 Ni-Cr 合金上, Ni-Cr 合金置于钢基体表面, 钎焊在 VAF-20 型真空炉中进行, 控制炉内真空度小于 10^{-2} Pa .

对腐蚀和电解后金刚石表面形貌采用日本电子公司(JEOL)JSM-6300 型扫描电镜(SEM)及美国 KEVEX 公司 X 射线能谱仪(EDS)进行分析, 相分析在日本 Shimadzu 公司 XD-3A 型 X 射线衍射仪上进行, 采用铜靶.

金刚石表面石墨化程度的测试采用法国 JOBIN YVON HR800UV 显微激光拉曼光谱仪, 试验用光栅为 600 gr/mm , 出射功率为 5 mW , 扫描范围为 $1\,000\sim 1\,700\text{ cm}^{-1}$. 测试采用波长为 514.5 nm 的激光线激发.

2 试验结果与分析

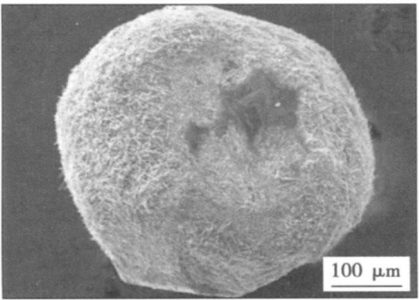
2.1 钎焊金刚石磨粒的表面形貌

图 1 是钎焊金刚石试样深腐蚀后金刚石的 SEM 形貌, 从图 1b 可以看出金刚石表面形成一层碳化物, 其微结构分析参见文献[3], 文中不再赘述.

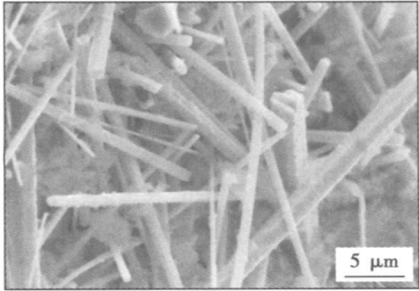
由于碳化物覆盖在金刚石表面, 且深腐蚀不能

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(a) 金刚石的整体形貌



(b) 表面碳化物形貌

图 1 腐蚀后的钎焊金刚石表面形貌

Fig. 1 Morphology of as-eroded brazed diamond

将之去除, 这影响了对金刚石表面石墨化的研究, 因此采用 20% (体积比) 稀硫酸溶液对金刚石试样进行电解处理, 将钎料层金属和碳化物去除.

图 2 为电解后钎焊金刚石表面的三维形貌. 从图中可以明显看出焊后金刚石仍然保持了焊前金刚石的整体轮廓形状, 但在金刚石的上部分表面有一层灰色凹凸不平的物质, 对该层物质进行能谱分析, 结果如图 3 所示.

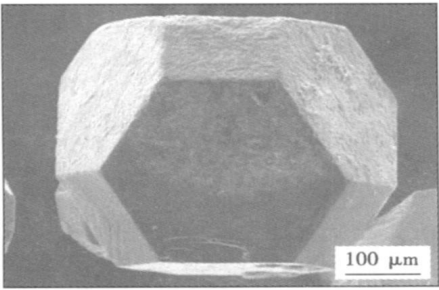


图 2 电解后的钎焊金刚石表面形貌

Fig. 2 Morphology of as-electrolyzed brazed diamond

从图 3 可知, 在金刚石表面除了残留的微量钎料成分 Ni, Si 元素以外, 主要为 C 元素. 图 4 为电解后金刚石表面生成物的三维形貌. 从图 4a 中可以明显看出有许多片层状的生成物在金刚石表面构成

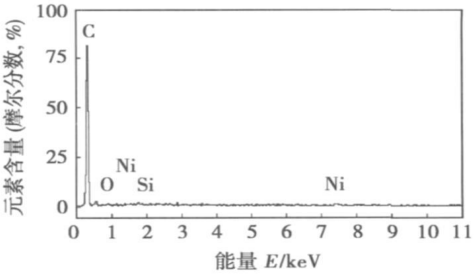
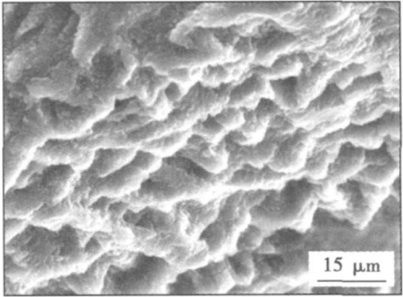


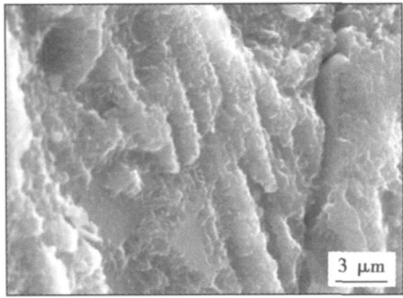
图 3 钎焊金刚石的表面能谱分析

Fig. 3 EDS of brazed diamond surface

网状形貌, 而从图 4b 中可以看出片层状生成物的厚度大约为 0.8 ~ 1 μm. 根据图 3 的能谱分析和图 4 生成物的表面形貌, 可以推测该生成物为片层状的石墨. 该层石墨片在金刚石磨粒表面叠合而成的平行塌陷片层构成了如图 4a 所示的网状孔洞.



(a) 网状石墨形貌



(b) 片层状石墨形貌

图 4 金刚石表面石墨形貌

Fig. 4 Morphology of graphite on surface of diamond

2.2 拉曼测试结果

虽然根据表面形貌和能谱分析可推测在金刚石的表面有石墨生成, 但是为准确判断该层物质的物相和该物相在金刚石表面生成的厚度, 采用 Raman 光谱对其进行研究. 金刚石和石墨为碳的同素异形体, 均由碳原子构成, 由于结构的差异, 导致了 Raman 散射谱的不同. 在金刚石中, C-C 键是 sp^3 杂化键, 形成正四面体结构, Raman 散射峰位于 1332 cm^{-1}

处;而石墨中C-C键是 sp^2 杂化键,形成平面层状结构,Raman散射峰位于 $1\,580\text{ cm}^{-1}$ 处,而微晶石墨在 $1\,355\text{ cm}^{-1}$ 处有一较强散射峰,这是由于散射发生在布里渊区边界的结果,非晶碳因结构上的无序性(包括键长和键角的无序),Raman散射峰是位于 $1\,530\text{ cm}^{-1}$ 附近的宽带。

测试方法如图5所示, H 为测量点距顶面的距离,分别进行了 $H=0, 5, 10\text{ }\mu\text{m}$ 处金刚石磨粒的Raman光谱频移的测试,图6为钎焊金刚石Raman光谱图。

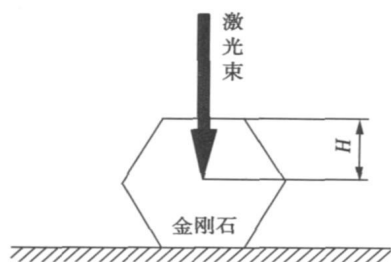


图5 Raman光谱测试金刚石示意图

Fig. 5 Measured position of Raman line-scan

从图6中可以看出,在 $1\,331.13\text{ cm}^{-1}$ 附近的Raman峰是 sp^3 结构的金刚石特征峰,在 $1\,355.15$ 和 $1\,585.05\text{ cm}^{-1}$ 附近观察到的较弱的Raman峰是 sp^2 结构的石墨,这说明在钎焊金刚石表面发生了石墨化。从图6中也可以看出,随着测试距离的增加,石墨特征峰的强度逐渐降低,在 $H=10\text{ }\mu\text{m}$ 处,石墨特征峰的强度已经非常微弱,再加大测试距离则测不到石墨的特征峰,只有金刚石的特征峰,这说明金刚石上生成的片状石墨厚度约为 $10\text{ }\mu\text{m}$,即只在金刚石表面发生了石墨化,金刚石没有发生整体的石墨化。

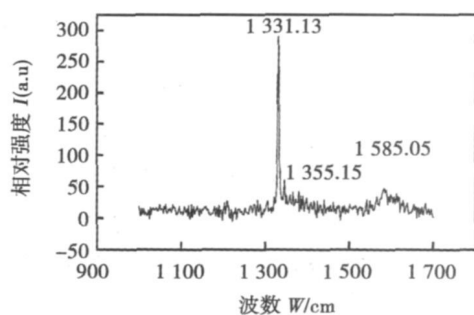
2.3 金刚石表面石墨化形成机理分析

金刚石在常温常压下是碳的亚稳同素异形体,金刚石之所以能保持其稳定的结构是因为晶格重构的动力学条件难以满足,但随着温度的升高,其动力学条件得以满足,而从热力学角度分析,金刚石转变为石墨Gibbs生成自由能 ΔG_T^0 为

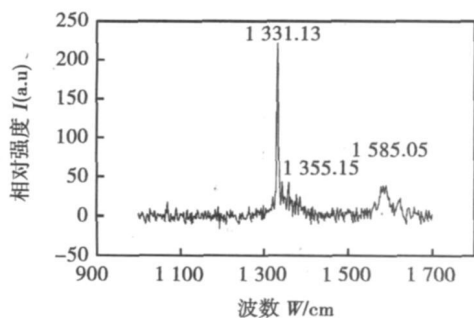
$$\Delta G_T^0 \leq -1\,100 - 4.64T \quad (1)$$

式中: T 为温度。Ni-Cr合金真空钎焊金刚石的温度高于 $1\,000\text{ }^\circ\text{C}$,此时金刚石石墨化的Gibbs自由能 $\Delta G_T^0 \leq -5\,740 \pm 50\text{ J/mol}$,说明金刚石具有较强的石墨化趋势,温度越高,反应趋势越大。在金刚石的表面或者缺陷部分(位错)由于能量比较高,更容易石墨化。

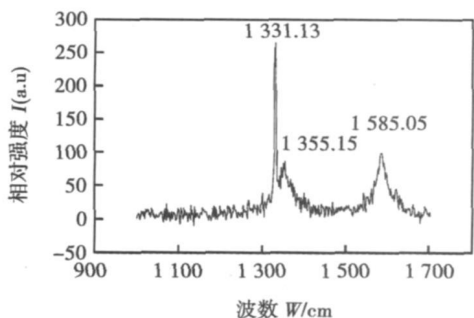
Ni-Cr合金真空钎焊金刚石时,在金刚石与Ni-



(a) $H=10$ 拉曼图谱



(b) $H=5$ 拉曼图谱



(c) $H=0$ 拉曼图谱

图6 钎焊金刚石的Raman光谱

Fig. 6 Raman spectra of brazed diamond

Cr合金固-液界面上镍的浸润作用结果将导致金刚石表面C原子向Ni-Cr合金熔体溶解和扩散,其实质是通过金刚石表层C原子 sp^3 结构被破坏、解体,解体后的 sp^2 状态C原子进入熔体的过程,随后表层下的 sp^3 结构变为表层也进行相同的解体破坏,如此循环下去金刚石的“溶解”是通过金刚石表面石墨化这一中间环节实现的^[8]。即在钎焊时,金刚石表面首先发生石墨化,随后才是石墨形式的C原子溶解于Ni-Cr合金钎料中,最后溶解的C和Cr原子生成如图1所示的碳化物,即碳化物的形成是石墨形式的C与Cr原子的反应产物,而不是金刚石上的C原子直接与Cr原子的反应产物。

由于金刚石石墨化的过程是逐步进行的,首先从被熔融Ni-Cr合金钎料浸润的金刚石的表面发生石墨化,随后才由表面向内部发展;而钎焊时间相对于金刚石整体石墨化的时间较短,因此金刚石只发

生了表面的石墨化,而不是整体的石墨化。

在随后的冷却过程中,由于 C 原子在镍中的固溶度随温度的降低而减小,如图 7 所示^[9],原来固溶在镍中的 C 原子将被析出,而在常温常压下,石墨是稳定相,因此析出的 C 原子便以石墨的方式存在于金刚石的表面。由于真空钎焊的冷却方式是随炉冷却,冷却速度相对缓慢,而在石墨型中相对缓慢凝固条件下,结晶的石墨以片状形态为主,根据 Gibbs-Curie-Wolf 晶体界面能理论^[10],晶体在结晶时,高能界面即悬空键强的界面具有高的生长速率,而低能界面生长速率小。石墨是各向异性差很大的晶体,构成基面的 C 原子彼此之间以共价键结合;在基面的片层之间以范德华键结合,石墨晶体棱面的界面能远高于基面的界面能,石墨在结晶时,若无其它因素影响,优先沿晶向生长,形成片状石墨,这就是如图 4 所示的金刚石表面片状石墨形成的原因。

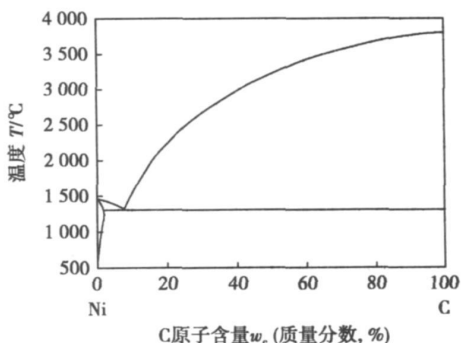


图 7 Ni-C 合金相图

Fig. 7 Ni-C phase diagram

从以上分析可知,石墨层的形成是由通过金刚石表面 C 原子结构的破坏、解体以及冷却过程中从 Ni-Cr 合金中析出形成的;采用 Ni-Cr 合金钎料真空钎焊金刚石时,首先在金刚石表面形成石墨层,随后才是碳化物层。

3 结 论

(1) 采用 Ni-Cr 合金钎料真空钎焊金刚石会导致金刚石表面的石墨化,其石墨层厚度约为 $10\ \mu\text{m}$,即只在金刚石表面发生了石墨化,金刚石没有发生整体的石墨化。

(2) 金刚石表面石墨化的原因是钎焊时金刚石表面 C 原子结构的破坏、解体以及冷却时 C 原子从

固溶体中的析出和再结晶。

(3) Ni-Cr 合金钎料真空钎焊金刚石时,首先在金刚石表面形成石墨,随后才是碳化物的生成。

参考文献:

- [1] Chattopadhyay A K, Chollet L, Hintemann H E. On performance of brazed bonded monolayer diamond grinding wheel[J]. Annals of the CIRP, 1991, 40(1): 347-350.
- [2] Chattopadhyay A K, Chollet L, Hintemann H E. Induction brazing of diamond with Ni-Cr hardfacing alloy under argon atmosphere[J]. Surface and Coatings Technology, 1991(45): 293-298.
- [3] 卢金斌, 徐九华, 徐鸿钧, 等. Ni-Cr 合金真空钎焊金刚石界面反应的热力学与动力学分析[J]. 焊接学报, 2004, 25(1): 21-24.
Lu Jinbin, Xu Jiuhua, Xu Hongjun, et al. Thermodynamic studies on interfacial reactions between diamond and Ni-Cr filler metal in vacuum brazing[J]. Transactions of the China Welding Institution, 2004, 25(1): 21-24.
- [4] Huang S, Fang T. Effects of brazing route and brazing alloy on the interfacial structure between diamond and bonding matrix[J]. Material Chemistry and Physics, 2004, 84(2): 251-258.
- [5] 臧建兵, 赵玉成, 王明智, 等. 超硬材料表面镀膜技术及应用(续)[J]. 金刚石与磨料磨具工程, 2000, 118(4): 7-12.
Zang Jianbing, Zhao Yuchen, Wang Mingzhi, et al. Technology and application of coating on superhard materials surface[J]. Diamond & Abrasives Engineering, 2000, 118(4): 7-12.
- [6] 姚裕成. 人造金刚石和超高压高温技术[M]. 北京: 化学工业出版社, 1996.
- [7] Jacob K T. Determination of the Gibbs energy of diamond using a solid state cell[J]. Solid State Communications, 1995, 94(9): 763-765.
- [8] 邓福铭. 超高压高温烧结中金刚石表面石墨化过程再研究[J]. 高压物理学报, 2001, 15(3): 235-239.
Deng Fuming. Graphitization process of diamond surfaces during the sintering of diamond-coalt system under high pressure and temperature[J]. Chinese Journal of High Pressure Physics, 2001, 15(3): 235-239.
- [9] Singleton M F, Nash P. Phase diagrams of binary nickel alloys[M]. USA: ASM International, Materials Park, 1991.
- [10] McSwain R H, Bates C E. 控制铸铁中石墨形成的表面能与界面能的关系[C] // 铸铁冶金学. 北京: 机械工业出版社, 1983: 280-284.

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Preparation and welding performance of amorphous interlayer alloys for TLP bonding ZHAI Qiuya¹, TONG Duxi¹, LI Weiwei², GONG Shaotao² (1. Xi'an University of Technology Materials Science and Engineering, Xi'an 710048, China; 2. Tubular Goods Research Center of Xi'an, Xi'an 710065, China). p 17—20

Abstract The composition and phase selection of Ni-Si-B amorphous interlayer alloys for transient liquid phase (TLP) bonding of 16Mn steel have been investigated. The TLP bonding experiment of 16Mn steels was conducted by a Gleeble-3500 thermal simulation testing machine, and the welding performance of the interlayer alloys, the interface microstructure and joint properties were analyzed. The results indicate that the amorphous Ni-6.8Si-(3—5)B interlayer alloys performs an excellent wettability and spreadability during TLP bonding. The joint gap is filled soundly and interfacial microstructure is uniform, which has no coarsening evidence compared with base metal. Under the experimental conditions of axial compressive load 10 MPa, temperature rising rate 50 °C/s, bonding temperature 1 150 °C, holding time 5 min., the joint bending angle reaches to 90°. Using amorphous Ni-based interlayer alloys can realize the higher strength TLP bonding of 16Mn steels.

Key words: 16Mn steel; TLP bonding; amorphous; interlayer alloy

Surface graphitization on brazed diamond with Ni-Cr alloy in vacuum brazing CHEN Yan, XU Hongjun, FU Yucan, SU Honghua (Jiangsu Key Laboratory of Precision and Micro-Manufacturing Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China). p 21—24

Abstract: The brazed diamond samples with Ni-Cr filler alloy were prepared by vacuum brazing method. The microstructure of graphite and the degree of graphite on diamond surface were analyzed by scanning electron microscope (SEM), energy dispersion spectrometer (EDS) and laser Raman spectroscopy. The results show that graphite grows on the surface of the diamond during vacuum brazing, diamond with Ni-Cr filler alloy and its thickness is about 10 μm. The reason of graphitization on brazed diamond surface is that there is degradation of atomic carbon on diamond surface in the molten Ni-Cr filler alloy during brazing, and there are precipitation and recrystallization of atomic carbon from the Ni-Cr filler alloy. The formation of graphite is earlier than the formation of carbide during vacuum brazing.

Key words: Ni-Cr alloy; vacuum brazing; diamond; graphitization

Residual stress evaluation of thin-plate LY12 by ultrasonic method and verification ZHANG Shiping¹, LU Hao², ZHU Zheng¹, FANG Hongyuan³ (1. School of Electrical Engineering and Automatic, Harbin Institute of Technology, Harbin 150001, China; 2. CSR Sifang Locomotive and Rolling Stock Company Limited, Qingdao 266111, Shandong, China; 3. State Key Laboratory of Advanced Welding Production Technology, Harbin Institute of Technol-

ogy, Harbin 150001, China). p 25—28

Abstract Residual stresses are one of the most important challenges to the safety of welded structures. Ultrasonic stress measurement installation was modified to meet the measurement of thin wall welded structure. The residual stress of LY12 body structure of high-speed train was measured by this system. The measurement process is not only nondestructive, but also real-time and quick. The measuring result of the ultrasonic method is verified by laser hologram interference hole-drilling method and finite element method. The deviations are also discussed.

Key words: ultrasonic; residual stress; nondestructive and quick; LCR wave

Finite element simulation of thermal stress on brazed K24 nickel-based joint ZHANG Lixia, FENG Jicai (State Key Laboratory of Advanced Welding Production Technology, Harbin Institute of Technology, Harbin 150001, China). p 29—32

Abstract By means of finite element method, maximum value of thermal stress and stress concentration zones of K24 nickel-based alloy joint brazed at 1 270 °C were simulated in this paper. The results show: during cooling process, the shear stress of K24 alloy joint concentrates at the interface tip and the maximum value of the shear stress appears at the right tip of Ni-based brazing alloy/K24 alloy interface, which decreases and then increases during cooling process. At the same time, the maximum value of stress in *x* direction of K24 alloy joint also appears on this site, which changes from negative to positive during cooling. After the temperature declines to room temperature, the joint seldom fractures in brazing alloy. Ni-based brazing alloy/K24 alloy interface easily becomes fracture zone as external force acts on the joint.

Key words: finite element simulation; K24 nickel-based alloy; residual stress; brazing

Simulation of effects of stand-off distance on explosive welding of three-layer tubes MA Bei, LI Hongwei, CHANG Hui, HU Rui (State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China). p 33—36, 40

Abstract Explosive welding is an advanced technology to achieve metallurgical bonding of dissimilar materials. Stand-off distance has a great effect on bonding quality. A 3D finite element model of explosive welding of steel/copper/copper three-layer tubes was established on the platform of ANSYS/LS-DYNA. The effects of stand-off distance on the explosive welding process and bonding quality were studied. The simulation results indicate that high bonding quality can be achieved when stand-off distance 1 and 2 is set to be 1/4—1 times of the thickness of flyer tube 1 and 1/2—2 times of the thickness of flyer tube 2 respectively. They do a little effect on the maximal plastic strain and the maximal effective stress of the bonded tube, which increase rapidly within 6 μs and then are stable. Stand-off distance 1 effects the movement of flyer tube 1 and flyer tube 2, while stand-off distance 2 only effects the movement of flyer