マテリアル先端リサーチインフラ利用報告書
ARIM User's Report

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課題データ / Project Data

課題番号 Project Issue Number	22KU0020
利用課題名 Title	In-situ high voltage transmission electron microscope study of the precipitation of Bi in primary Sn dendrites in Sn-Bi low temperature solder alloys
利用した実施機関 Support Institute	九州大学 / Kyushu Univ.
機関外・機関内の利用 External or Internal Use	外部利用/External Use
横断技術領域 Cross-Technology Area	計測・分析/Advanced Characterization
重要技術領域 Important Technology Area	次世代ナノスケールマテリアル/Next-generation nanoscale materials
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利用者と利用形態 / User and Support Type

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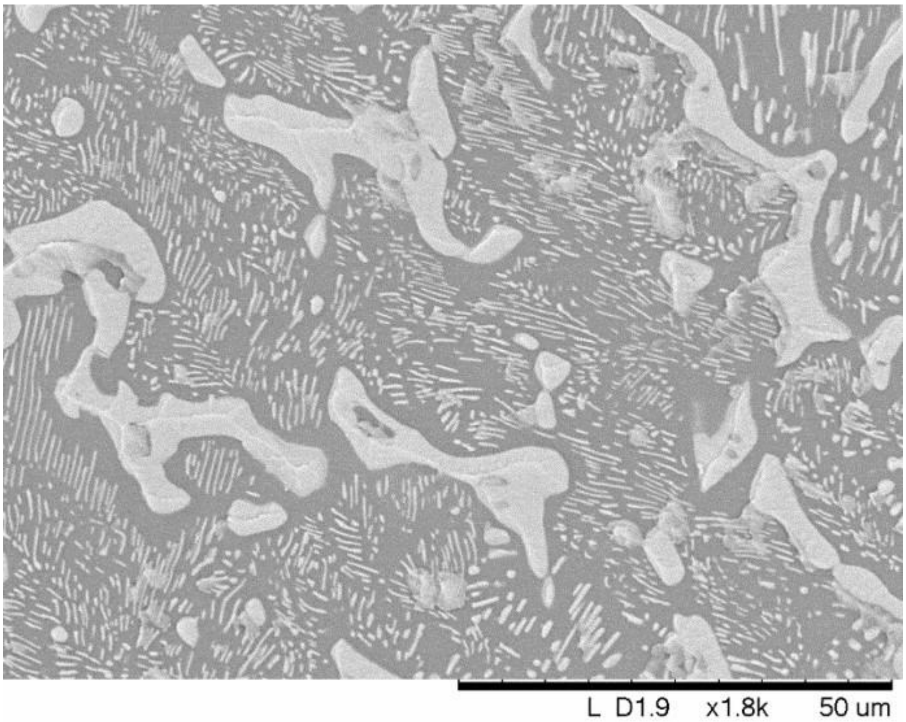
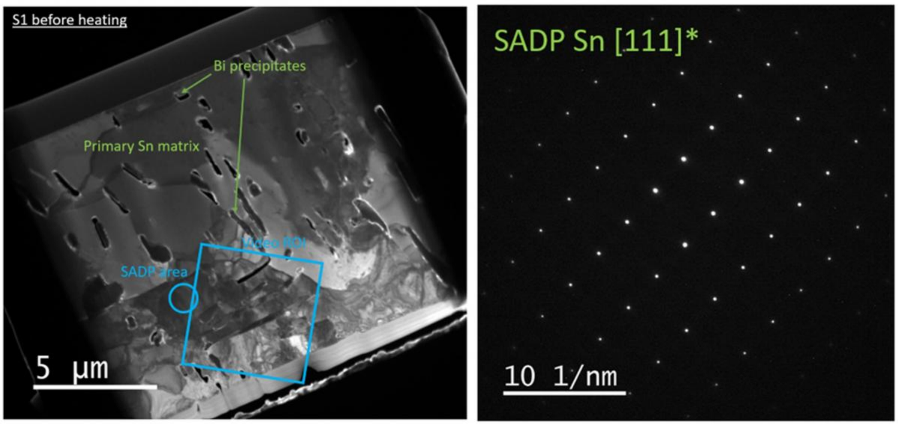
利用形態 Support Type	技術補助/Technical Assistance

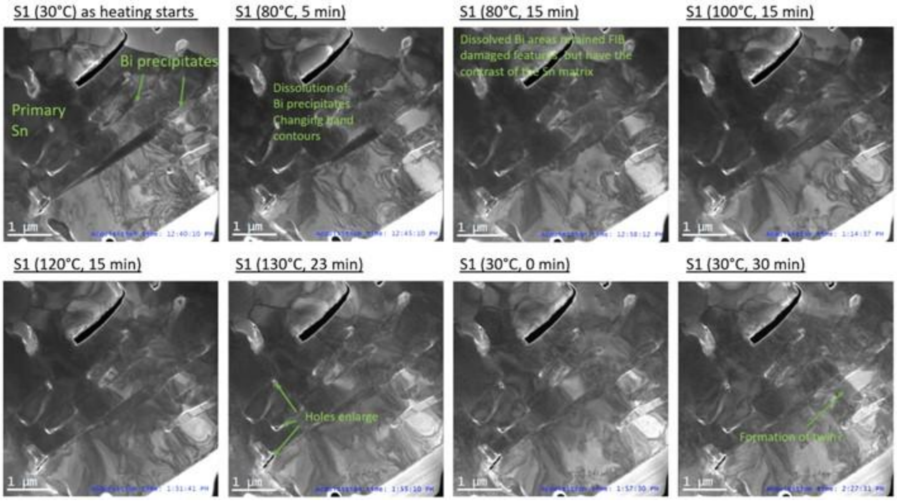
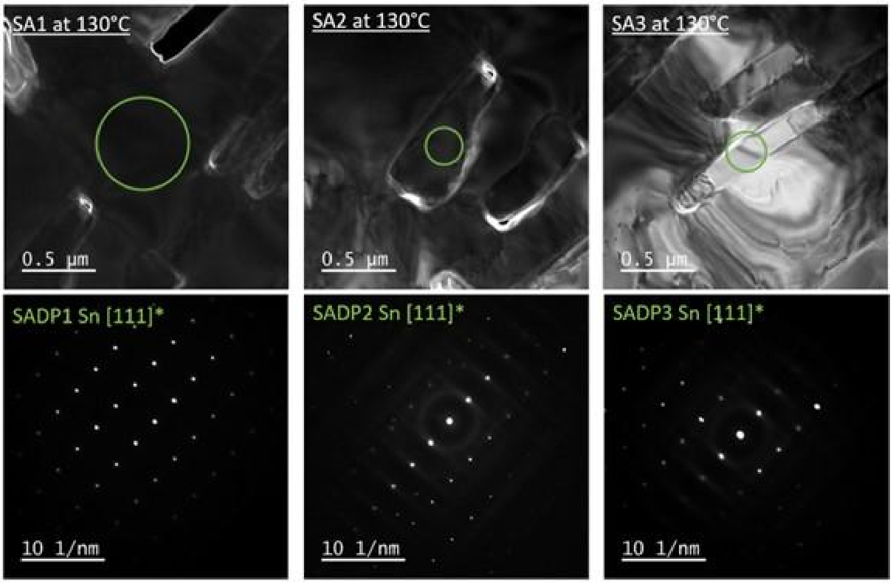
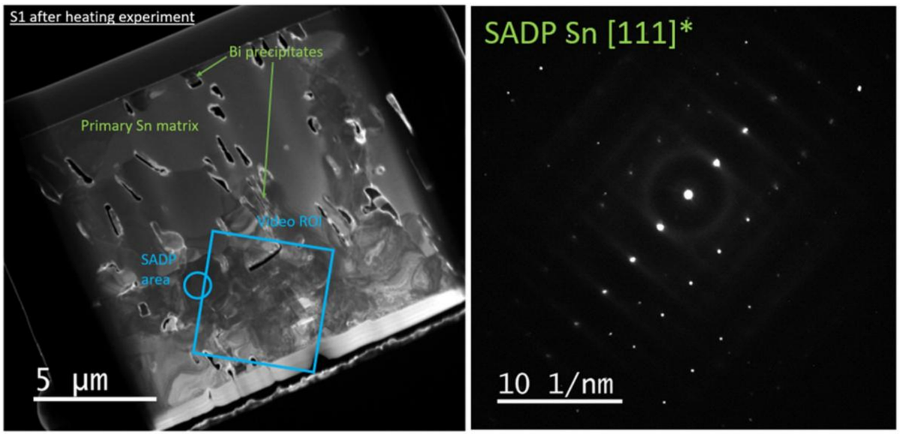
利用した主な設備 / Equipment Used in This Project

利用した主な設備 Equipment ID & Name	KU-001：電子分光型超高圧分析電子顕微鏡

報告書データ / Report

概要（目的・用途・実施内容） **Abstract (Aim, Use Applications and Contents)**	The development of low temperature solders are driven by environmental, costs and technical reasons to reduce the temperature during the electronic manufacturing processes. Lower soldering temperatures can reduce the process energy and costs, while also reduces thermal damage to temperature sensitive electronic components and thermally induced mechanical stresses [1-2]. Sn-Bi is identified and prioritized as the most promising low temperature solders [3-4]. However, due to the low melting point, the Sn-Bi solders are operating close to their melting point. As a result, solid state processes such as diffusion proceed at faster rates than in conventional solder alloys. Also, the solid solubility of constituent elements varies widely over that normal range of operating temperatures [5]. One consequence is that fine Bi precipitates in the Sn dendrite over time only to redissolve when the temperature increases during operation of the circuitry. Electronic manufacturers have found these issues compromise reliability in service. Therefore, the aims of this experiment are: To study the kinetics of fine Bi precipitation at temperatures relevant to low temperature soldering applications. To study the solubility of Bi in Sn at these temperatures.
実験 **Experimental**	1.1 Sample fabrication: A Sn-37wt%Bi alloy characterised by significant quantities of both independent Sn phases and Sn-Bi eutectic phases (Fig. 1.) is used for this experiment. The sample was prepared by alloying Sn and Bi (99.9% purity) in a crucible at 400℃ for 1 hour, and casting the sample into cylindrical moulds of 10 mm in diameter. The cast sample was cut into 20 mm lengths, mounted in epoxy resin and the surface was polished with standard metallography procedures. Transmission electron microscopy (TEM) lamellae was cut out from the polished sample with a focused-ion-beam (FIB) technique. The sample was thinned to 500 nm to prevent excessive FIB damage to the temperature sensitive Sn-Bi alloys. 1.2 In-situ heating high voltage transmission electron microscopy (HV-TEM)The TEM experiment was conducted on the High voltage TEM (HV-TEM) JEOL JEM-1300NEF with an accelerating voltage of 1,250 keV. The TEM lamellar was placed on a double-tilt JEOL EM-HSTH heating TEM holder. The sample was heated stepwise to temperatures relevant to the production and service temperatures of solder alloys, and time dependent microstructural changes, in particular the dissolution of fine Bi in the primary Sn dendrite during heating, was captured in a video. The following experimental procedures was used: • Tilt to the zone axis of Sn • Take image and diffraction pattern of ROI • Start Video 1 • Heat sample to 80℃ at 20℃/minute, hold 15 minutes and observe dissolution of Bi • Heat sample to 100℃ at 20℃/minute, hold 15 minutes and observe dissolution of Bi • Heat sample to 120℃ at 20℃/minute, hold 15 minutes and observe dissolution of Bi • Heat sample to 130℃ at 20℃/minute, hold 10 minutes and observe dissolution of Bi • Stop Video 1, continue to hold at 130℃, take images, check diffraction patterns of dissolved Bi areas • Start Video 2 • Cool sample to 30℃ (cooling rate uncontrolled) • Hold 30 minutes and observe precipitation of Bi • Stop Video 2

結果と考察 **Results and Discussion**	Fig. 2a shows the TEM lamellar before the heating experiment. The lamellar is tilted to the zone axis of the matrix of single crystal primary Sn. The diffraction pattern of the SADP area marked on Fig. 2a is shown in Fig. 2b, consistent with the pattern of the Sn [111] axis. Bi precipitates in the primary Sn are also visible in Fig. 2a. Fig. 3 shows the snapshots taken from Video 1 as the sample was heated. Dissolution of Bi precipitates was visible after 5 minutes at 80℃, resulting in the change in band contours. Bi continued to dissolve after 15 minutes at 80℃. The dissolved Bi areas have the contrast of the Sn phase but retained the FIB damaged features. At 130℃, holes at the Sn/Bi interface began to enlarge. SADPs at 130℃ shows the Bi precipitates have dissolved, sharing the same pattern as the Sn matrix (Fig. 4). The TEM lamellar after the heating experiment is shown in Fig. 5a. The sample is still on-zone of the single crystal primary Sn matrix (Fig. 5b).
図・表・数式 1 **Figures, Tables and Equations 1**	 Fig. 1. Sn-37wt%Bi alloy showing fine Bi precipitates (brighter phase) in the independent Sn phase (darker phase), and the eutectic Sn-Bi phases.
図・表・数式 2 **Figures, Tables and Equations 2**	 Fig. 2. (a) Image of the TEM lamellar before the heating experiment. (b) SADP of the area marked in (a).

図・表・数式 3 **Figures, Tables and Equations 3**	 Fig. 3. Snapshots of the ROI during the in-situ heating TEM experiment at different temperatures and times.
図・表・数式 4 **Figures, Tables and Equations 4**	 Fig. 4. SADPs taken at 130˚C showing Bi had dissolved into Sn.
図・表・数式 5 **Figures, Tables and Equations 5**	 Fig. 5. (a) Image of the TEM lamellar after the heating experiment. (b) SADP of the area marked in (a).

その他・特記事項（参考文献・謝辞等） Remarks(References and Acknowledgements)	Funding: This work was supported by The University of Queensland, Australia [Knowledge Exchange & Translation fund 2021002690]; Nihon Superior Co., Ltd, Japan [2016001895, 2021002341]; Australian Research Council, Australia [DP200101949]; and ANSTO, Australia [AS211/PD/16842]. [1] Kang, H., S.H. Rajendran, and J.P. Jung, Low Melting Temperature Sn-Bi Solder: Effect of Alloying and Nanoparticle Addition on the Microstructural, Thermal, Interfacial Bonding, and Mechanical Characteristics. Metals, 2021. 11(2): p. 364. DOI: 10.3390/met11020364.[2] Wang, F., et al., Recent progress on the development of Sn–Bi based low-temperature Pb-free solders. Journal of Materials Science: Materials in Electronics, 2019. 30(4): p. 3222-3243. DOI: 10.1007/s10854-019-00701-w.[3] Fu, H., et al. iNEMI project on process development of BISN-based low temperature solder pastes — Part II: Characterization of mixed alloy BGA solder joints. in 2018 Pan Pacific Microelectronics Symposium (Pan Pacific). 2018. DOI: 10.23919/PanPacific.2018.8318989.[4] Scott Mokler, et al. The application of Bi-based solders for low temperature reflow to reduce cost while improving SMT yields in client computing systems. in SMTA International. 2016. Rosemont, IL, USA. [5] Hao, Q.C., et al., The Effects of Temperature and Solute Diffusion on Volume Change in Sn-Bi Solder Alloys. JOM, 2022. 74(4): p. 1739-1750. DOI: 10.1007/s11837-021-05145-4.

成果発表・成果利用 / Publication and Patents

DOI（論文・プロシーディング） DOI (Publication and Proceedings)	
口頭発表、ポスター発表および、その他の論文 Oral Presentations etc.	
特許出願件数 Number of Patent Applications	0件
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