Journal of Alloys and Compounds 821 (2020) 153488

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Metastable microstructures in the solidification of undercooled high entropy alloys

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ARTICLE INFO

Article history:
Received 13 September 2019
Received in revised form
18 December 2019
Accepted 20 December 2019
Available online 21 December 2019

Keywords:
Undercooling
High entropy alloys
Phase field simulation
Micro-segregation

ABSTRACT

High entropy alloys with multiple phases are taken for undercooling studies and established the microstructure evolution with respect to undercooling. The melt fluxing technique was used for the current study to achieve undercooling. Predictions on the equilibrium phase formation of these systems was performed using CALPHAD approach and compared with experimental observations. Metastable microstructures were observed during undercooling and the morphological changes could be correlated with the currently established mechanisms. The detailed microstructure evolution in $FeCoNiCuX_{0.5}$ (X = Al, Mo, Ti, W, Zr) shows the minute addition of these elements results in variation in microstructure evolution during as cast as well as undercooled condition. The studied systems show a maximum undercooling of more than 0.18 T_L and maintained crystalline nature even in deep undercooling. The segregation nature of elements was studied and correlated with the phase field simulations obtained.

1. Introduction

Development of high entropy alloys or multi principle element alloys leads to the exploration of new alloy combination at the centre of the phase diagram [1–3]. Recent reports show that HEA stability or properties are depending on the type of elements and its composition [4,5]. Entropy stabilisation irrespective of the type of elements taking part in these alloy formation is no longer valid for microstructure evolution and properties [6]. Open literature shows that based on the type of elements different microstructure combinations can be achieved in HEAs such as eutectic HEAs [7,8], high entropy superalloys [5] and multi-phase HEAs [9]. The recent reports show multi-phase alloys with high entropy phases also reported by properly optimising the composition domain [10]. The type of elements can also effect the solidification behaviour of HEAs [11]. During development of novel HEAs it is necessary to take the processing conditions into account.

Solidification studies by undercooling multi-component equiatomic alloys are limited in open literature [12,13]. By controlling the undercooling, different morphological variation as well as phase selection can be obtained. Such changes in microstructures of model alloy systems such as Ni-Cu [14] and Fe–Ni [15] as a function of undercooling are well documented. The growth kinetics can also be modified with minute additions of certain solute elements in metals [16]. Such reports on minute addition of solute elements and their effect on microstructure evolution of HEAs are not available in the open literature.

In this study, FeCoNiCu system was selected for undercooling studies with minute addition of solute such as Mo, Ti, Al, W, Zr. All the systems are undercooled to various undercooling levels using melt fluxing method. The morphological variation of undercooled sample samples with respect to undercooling was summarised. Phase field modelling was carried out in these systems to assess the prediction capability for segregation behaviour in the undercooled condition.

2. Experimental and simulation details

The samples of the required composition were arc melted using vacuum arc melting technique. Elemental pure metals (>99.99%) were taken in required proportions and melted using an electric arc struck between the non consumable Tungsten electrode and a water cooled copper mould. The melted button was flipped and melted six times to get the homogeneous microstructure throughout the sample. The arc melted button was cut into

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https://doi.org/10.1016/j.jallcom.2019.153488
0925-8388/

required dimensions for the undercooling experiments using melt fluxing technique. The flux used was boron trioxide which covers the whole sample and avoids nucleation sites. The experiments were carried out in an argon atmosphere and the temperature of the sample was measured *in-situ* by a non-contact two-colour pyrometer. The undercooled sample was metallographically prepared for further characterisation. The microstructure and EDS analysis were performed in backscattered electron mode in scanning electron microscopy (Quanta 400® and InspectF® from FEI®).

Undercooled sample microstructure simulation was carried out using Micress® software. The Multi phase field model was used in the software which can handle multiple-phase evolution. In the current solidification study, only two phases were chosen for simulation: one is solid primary phase and the other is the liquid phase. The phase field order parameter will take a value of 1 for solid phase and 0 for the liquid and changes smoothly between the two phases. The thermodynamic data for the simulation was taken from Thermo-Calc® and the real-time calculation was enabled by TQ® interface. The database used for the current study was TCHEA2. The kinetic data such as diffusion values were optimised for the alloys taking into consideration of the order of magnitude was similar to dilute alloys such as Fe based alloys. The formulation for the multiphase field and diffusion equation was explained elsewhere [17,18].

3. Results and discussion

3.1. Thermodynamic prediction and as-cast sample

The as-cast sample prediction was shown in Fig. 1 where the Scheil's solidification pathway shows FeCoNi rich primary FCC phase formation. The SEM BSE image confirms that the as-cast sample in $FeCoNiCuMo_{0.5}$ consists of predominantly a primary dendritic phase and a segregated interdendritic region. The EDS point analysis shows the composition of each phase in the studied alloy sets. The primary dendritic phase is enriched with FeCoNi as per the Thermo-Calc® prediction. The interdendritic region is enriched with Cu. Mo has a negative enthalpy of mixing with Fe, Co, Ni so is expected to segregate in the dendritic region compared to interdendritic region where it has a positive enthalpy of mixing with Cu [19,20]. The as-cast EDS compositional analysis shows that the Mo enrichment in the primary dendritic phase. The behaviour of Mo partitioning in undercooled condition was verified by experimentally and simulation condition was shown in subsequent section. Ti has a high negative enthalpy of mixing with Fe, Co, Ni and Cu is thus expected to partition either into one of the phases or form as a separate phase. The EDS results on as-cast sample show that the Ti is getting enriched in the interdendritic region. The extent of partitioning of Ti in undercooled condition was verified by using phase field simulation.

3.2. Thermal cycle for undercooling studies

Fig. 2 shows the thermal cycle at the cooling portion of undercooling experiments of $FeCoNiCuMo_{0.5}$ alloy. The recalescence in the thermal cycle due to the latent heat coming out because of primary phase formation. The liquidus temperature measured from low undercooling experiments and not from the differential

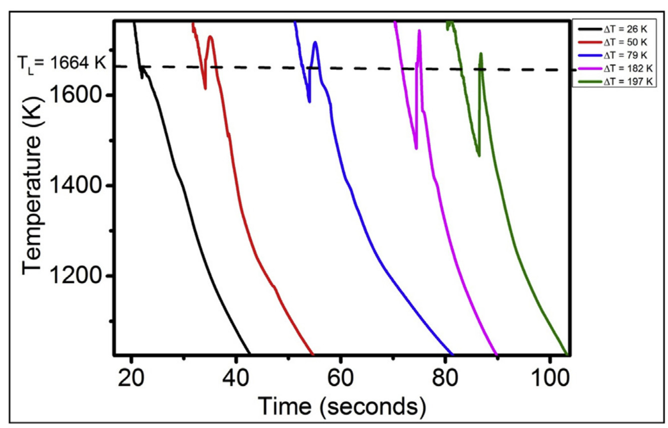
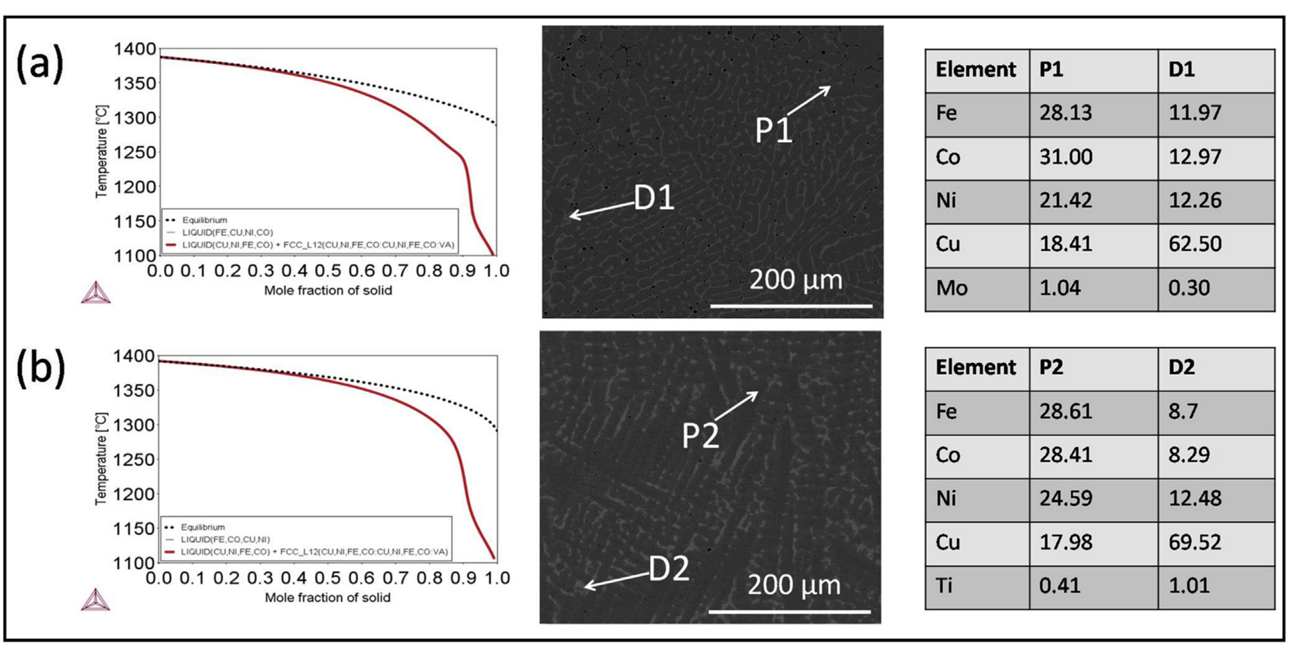


Fig. 2. Thermal cycle of undercooling experiments in $FeCoNiCuMo_{0.5}$ alloy.



Element	P1	D1
Fe	28.13	11.97
Co	31.00	12.97
Ni	21.42	12.26
Cu	18.41	62.50
Mo	1.04	0.30

Element	P2	D2
Fe	28.61	8.7
Co	28.41	8.29
Ni	24.59	12.48
Cu	17.98	69.52
Ti	0.41	1.01

Fig. 1. Thermo-Calc® prediction, BSE-SEM images and EDS compositional analysis of as cast a) $FeCoNiCuMo_{0.5}$ and b) $FeCoNiCuTi_{0.5}$ alloys.

scanning calorimetry experiments. However, this liquidus is comparable to the estimate from the Thermo-Calc® database. The discrepancy of the liquidus versus maximum temperature after recalescence could be due to local composition changes, non-equilibrium effects or measurement errors such as local emissivity changes. The thermal cycle also confirms there is no other recalescence event happening in this system which ensures that there is no other phase transformation during cooling.

3.3. Microstructure evolution of undercooling $FeCoNiCuMo_{0.5}$ alloy: Experiments and simulation

Fig. 3 shows the backscattered SEM images of undercooled $FeCoNiCuMo_{0.5}$ alloy at various undercooling regimes. Dendritic morphology was predominant up to an undercooling of 26 K. The grain + dendrite morphology was obtained at an undercooling range of 26–50 K. This grain morphology was due to the dendrite remelting that occurs during recalescence event. The fraction of remelting in this undercooling zone is such a way that the solid fraction is more than 0.8 which causes the finally solidified segregated Cu surrounds the grains. This kind of observation was reported for binary alloys such as Ni–Cu and Fe–Ni systems [15,21]. From 50 to 79 K undercooling the columnar morphology was predominantly observed. From 79 to 182 K undercooling we can see a mixture of columnar dendrite and grain or cellular morphology. Above 182 K undercooling the grain or cellular morphology was observed which may due to recrystallization because of stress accumulated by volume change during rapid solidification.

Fig. 4 shows the phase field simulation results at an undercooling of 73 K. The phase field plot and Cu composition profile with single dendrite was shown which confirms that Cu is segregated in the interdendritic region. The extent of copper segregation in interdendritic and grain boundary was simulated with multiple dendrites of different orientation and compared with the experimentally obtained EDS mapping of Cu. The line scan EDS profile obtained from simulation and experiments confirms that the phase field simulation predicts the compositional profile of other components accurately. The minute Mo addition gets segregated in the dendrite region which was shown in experimental as well as the predicted line scan profile. From these studies, one can conclude that the microstructure simulation with a suitable experimental condition can able to predict the segregation behaviour of constituent elements even in minute quantity. The capability can be used for microstructure prediction high entropy alloys during manufacturing condition.

3.4. Microstructure evolution of undercooling $FeCoNiCuTi_{0.5}$ alloy: Experimental and simulation

The morphological variation of undercooled $FeCoNiCuTi_{0.5}$ was shown in Fig. 5a. Where dendritic morphology was observed up an undercooling of 41 K. Columnar dendritic morphology was shown at a range of 41–151 K undercooling. Grain morphology observed between 151 K and 155 K could be attributed to dendrite remelting. Columnar dendrite morphology was observed at an undercooling rage of 155–208 K and grain or cellular morphology was observed $\Delta T > 208$ K. The phase field simulation plot with line scan data are shown in Fig. 5b which confirms that the Co, Ni getting enriched in the primary dendritic phase and Cu getting enriched in the interdendritic region. It is to be noted that from EDS line scan on simulation results show the Ti getting enriched in the interdendritic region.

3.5. Summary of morphological variation $FeCoNiCuX_{0.5}$ alloy

Fig. 6 shows the morphological variation due to undercooling in $FeCoNiCuX_{0.5}$ alloy with various solute content. Apart from the effect of Mo and Ti other elements such as W, Zr, Al is shown in Fig. 6. The minute W addition will result in liquid phase separation where a W–Fe rich phase will form (supplementary file) and it appears as globules in the sample. The liquid phase separation was observed in as-cast condition which is continued in undercooled samples too. The primary phase morphology changes from dendrite to columnar dendrite then to dendrite + grain morphology with respect to increase in undercooling. The Zr addition shows the dendrite, columnar dendrite, irregular crystal, columnar dendrite and grain or cellular morphology while an increase in undercooling. Zr containing sample got the highest

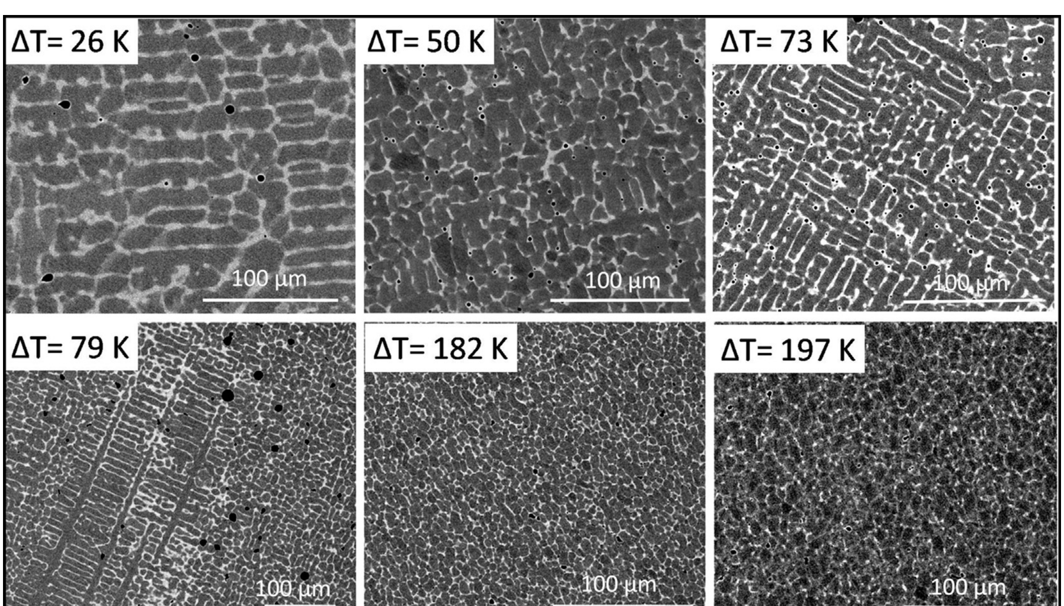


Fig. 3. BSE SEM images of undercooled $FeCoNiCuMo_{0.5}$ alloy at various undercooling domain.

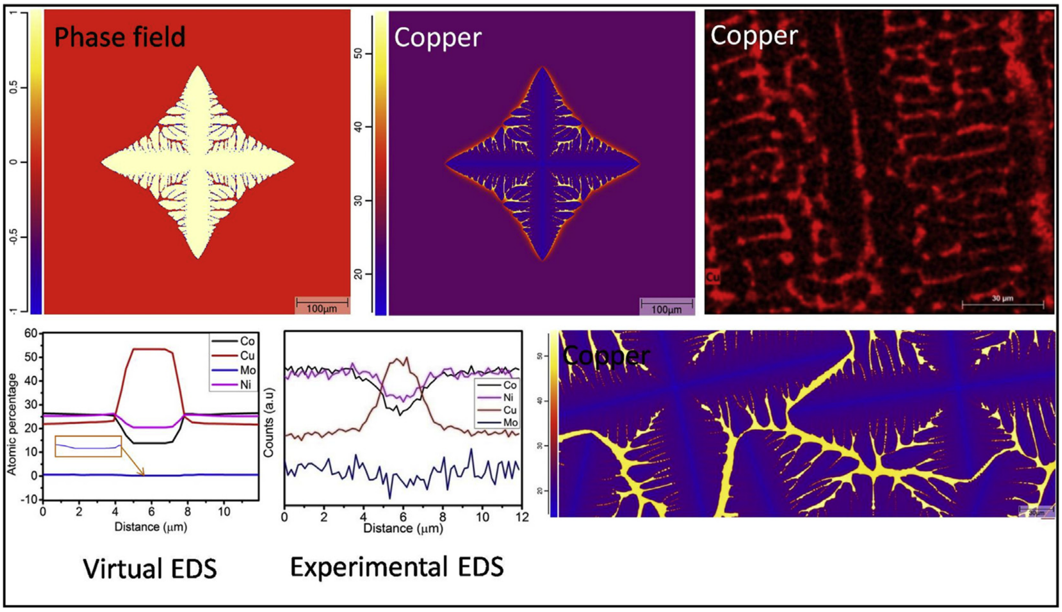


Fig. 4. Comparison of experimental and simulated compositional profile of undercooled $FeCoNiCuMo_{0.5}$ alloy at 73 K undercooling (The colour code shown in compositional profile is in atomic percentage). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

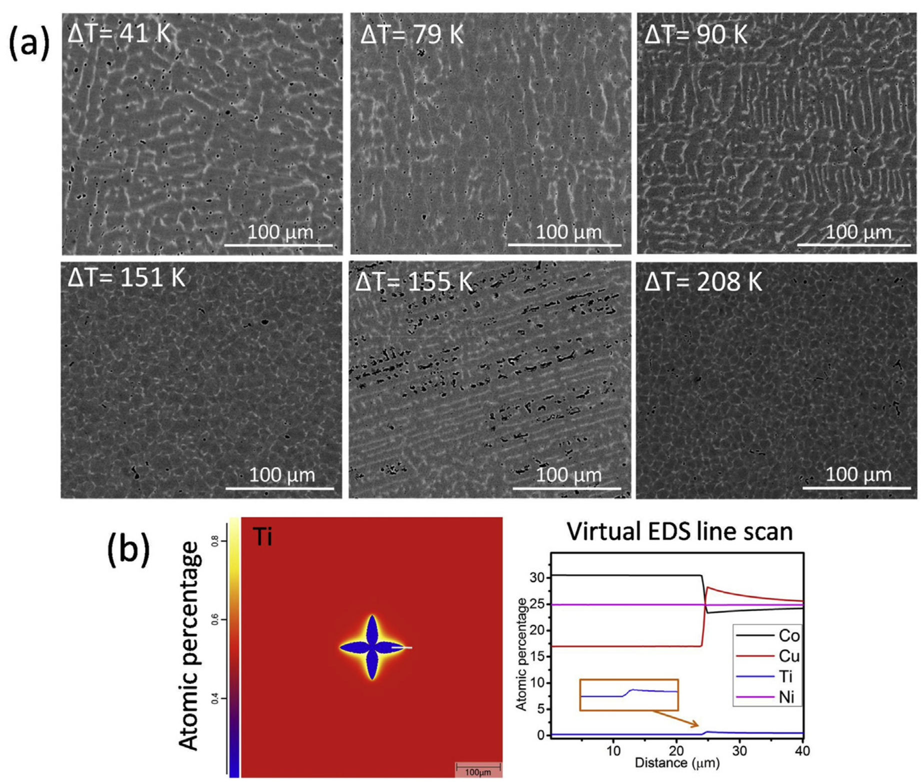


Fig. 5. a) BSE SEM images of undercooled $FeCoNiCuTi_{0.5}$ alloy at various undercooling domain, b) Compositional plot of Ti and line scan along the tip of dendrite at an undercooling of 79 K.

undercooling of 368 K and even in these deep undercooling also the sample is crystalline (supplementary file). The Al containing sample shows morphology variation similar to Zr containing alloy but undercooling ranges are different. From these studies, it can be concluded that the morphology variation will depend on not only undercooling obtained but also the minute solute addition. Like diffusion studies, the solidification studies in undercooled condition points out that the type of elements will affect the phase formation and morphology variation even though high configuration entropy exists. The degree of deep undercooling obtained was depend upon the minute solute addition and its characteristics.

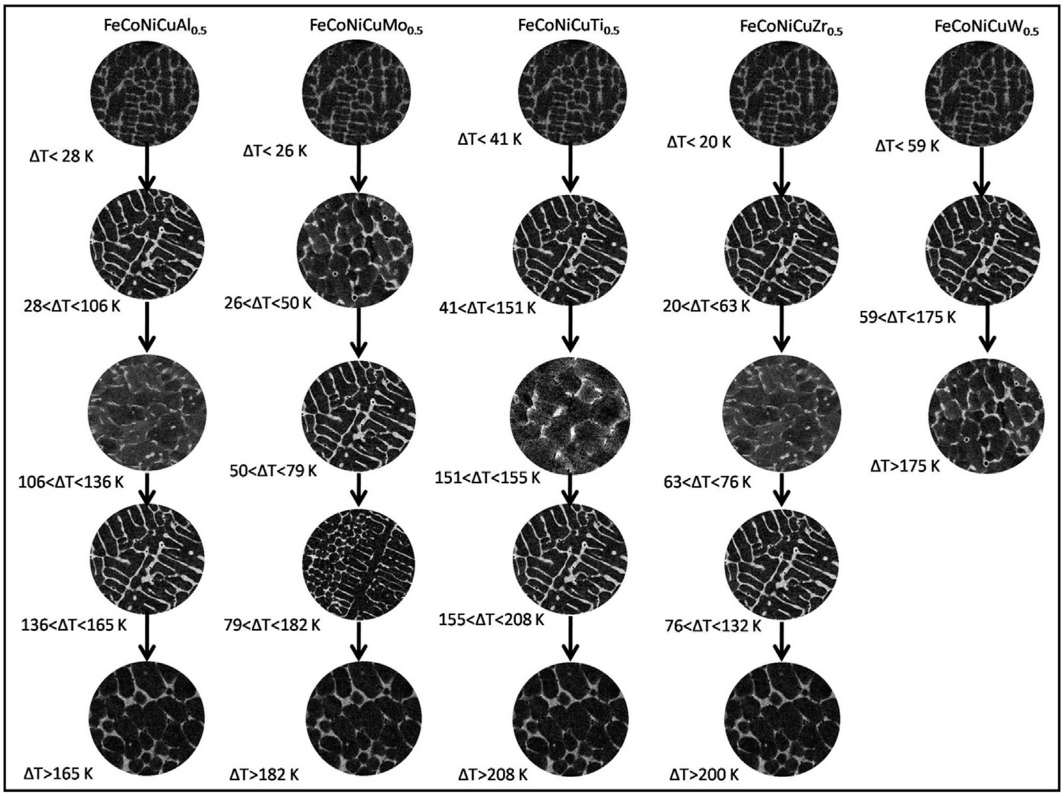


Fig. 6. Summary of morphological variation with respect undercooling of studied $FeCoNiCuX_{0.5}$ system.

4. Conclusions

Undercooling studies on $FeCoNiCuX_{0.5}$was carried out using melt fluxing technique shows morphological variation based on the undercooling obtained and solute addition. Liquid phase separation was observed in W containing alloy whereas crystalline nature was observed for Zr containing alloy even in deep undercooling of 368 K. The effect of type of element and its minute addition need to be considered for alloy design and development of HEAs. Phase field method can be used to predict the segregation behaviour including the effect of minute solute addition in multi-component equiatomic alloys.

CRediT author contribution statement

Rahul M R: Investigation, Formal analysis, Software, Writing - Original Draft. **Sumanta Samal:** Investigation, Formal analysis, Writing – Review. **Gandham Phanikumar:** Resources, Methodology, Conceptualization, Writing - Review & Editing, Validation, Funding acquisition, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jallcom.2019.153488.

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