

Electronic supplementary information (ESI)

“Chemical origin of differences in steel corrosion behaviors of *s*-electron and *p*-electron liquid metals by first-principles calculation”

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A Determination of initial configuration and spin condition

This section describes how the initial configuration of FPMD simulation and the spin configuration of the ground state were determined for each impurity-containing liquid Na system. First, three atomic configurations were randomly selected from the trajectories of the pure liquid Na simulation. After selecting the configuration candidates, one Na atom was randomly replaced with a *3d*-transition metal (*3d*-TM) impurity. Subsequently, a single point calculation was performed for each configuration with and without the spin-polarized condition. If there were no magnetic moments and no energy differences even if the spin-polarized calculation was performed, we decided to switch off the spin-polarized condition because the ground state was considered to be non-magnetic.

Table S1 presents the magnetic moment and system energy of the single point calculation with and without spin-polarized condition for each *3d*-TM impurity-containing liquid Na system. From Sc to Ni impurity, a non-zero magnetic moment is induced under the spin-polarized condition, and the system energy is lower than without the spin-polarized condition. Thus, we concluded these systems should have a magnetic moment in the ground state. In contrast, Cu- and Zn-containing systems do not have magnetic moments even when the spin-polarized condition is switched on. In addition, there is no difference in the system energy with and without the spin-polarized condition. Thus, we decided to switch off the spin-polarized condition for Cu- and Zn-containing systems because non-magnetic states are the ground states. Even when we conducted a short FPMD simulation for Cu- and Zn-containing systems with the spin-polarized condition, no magnetic moment was induced.

Table S1. Magnetic moment and system energy of the single point calculation with and without spin-polarized condition for impurity-containing systems. The gray shaded combination (atomic configuration and spin condition) for each system was chosen as the initial configuration and spin condition of the FPMD simulation because the system energy was the lowest among six test cases (three configurations with and without the spin-polarized condition).

Impurity-containing liquid Na system		Configuration-1		Configuration-2		Configuration-3	
		Magnetic moment (μ_B)	System energy (eV)	Magnetic moment (μ_B)	System energy (eV)	Magnetic moment (μ_B)	System energy (eV)
Sc	with spin	1.51	-116.64	1.58	<u>-117.58</u>	1.35	-116.77
	w/o spin	0	-116.58	0	-117.47	0	-116.72
Ti	with spin	3.11	-117.13	3.10	<u>-118.06</u>	2.97	-117.30
	w/o spin	0	-116.38	0	-117.23	0	-116.56
V	with spin	4.46	-118.13	4.47	<u>-119.04</u>	4.39	-118.32
	w/o spin	0	-116.16	0	-116.99	0	-116.37
Cr	with spin	5.14	-119.44	5.12	<u>-120.43</u>	5.16	-119.65
	w/o spin	0	-115.98	0	-116.87	0	-116.20
Mn	with spin	4.64	<u>-120.04</u>	4.63	-119.05	4.69	-119.27
	w/o spin	0	-116.80	0	-115.87	0	-116.12
Fe	with spin	3.14	-117.54	3.19	<u>-118.47</u>	3.30	-117.90
	w/o spin	0	-115.75	0	-116.95	0	-115.02
Co	with spin	2.27	<u>-117.22</u>	2.06	-116.15	1.59	-116.44
	w/o spin	0	-116.44	0	-115.61	0	-116.00
Ni	with spin	0.29	<u>-116.46</u>	0.71	-115.51	0.27	-115.65
	w/o spin	0	-116.27	0	-115.37	0	-115.64
Cu	with spin	0.00	-114.81	0.00	-115.82	0.00	-115.10
	w/o spin	0	-114.81	0	<u>-115.82</u>	0	-115.10
Zn	with spin	0.00	-113.08	0.00	-114.14	0.00	-113.34
	w/o spin	0	-113.08	0	<u>-114.14</u>	0	-113.34

B Convergence of total energy, pressure, and PCF

In Section 2 of the main body, the equilibration time was determined to be 5 ps based on the convergence of the total energy, pressure, and pair-correlation function (PCF) of the systems. As supporting data, the data used when determining equilibration time are presented for three typical systems: Cr- (magnetic system) and Cu-containing (non-magnetic system) and pure liquid Na.

(1) The system energy and pressure

Fig. S1 shows the time evolution of system total energy and pressure for (a) pure Na and (b) Cr- and (c) Cu-containing Na systems. In each figure, the black and red horizontal lines indicate the averaged system energy and pressure from 5 ps to 30 ps, respectively. In Fig. S1(a), the total energy and pressure at the beginning of the simulation are very low, indicating that the initial configuration was unrealistic for liquid Na. However, the values immediately increase and fluctuate near the horizontal lines. For Cr- and Cu-containing Na systems, the values fluctuate around the equilibrated values without immediate increase, since the initial configuration was reasonably close to equilibrium as it was prepared from an equilibrated pure Na configuration. These results indicate the system energy and pressure were reasonably equilibrated within 1 ps.

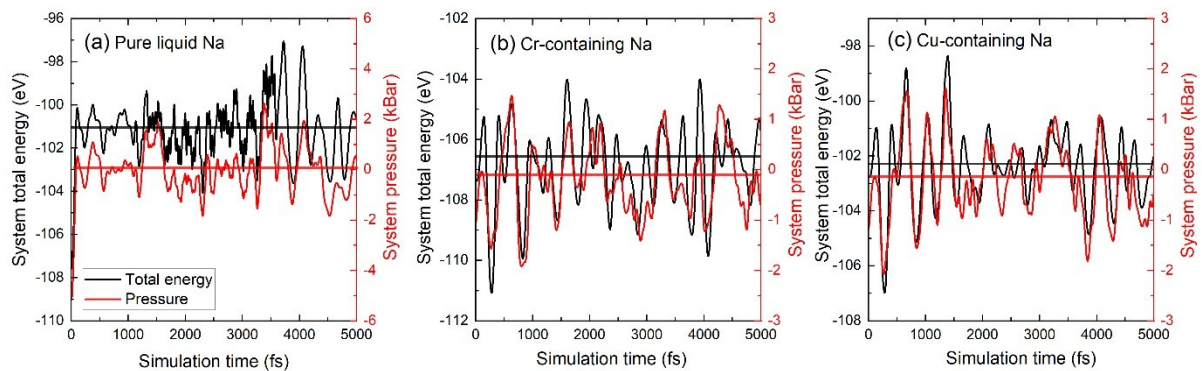


Fig. S1. The system total energy and pressure of (a) pure Na and (b) Cr-, and Cu-containing Na systems as a function of simulation time.

(2) The geometric factor, PCF

In addition to the convergence of system energy and pressure, we further evaluated the convergence of geometric factor, PCF. Fig. S2 illustrates (a) PCF of Na, partial PCF of (b) Cr-impurity and (c) Cu-impurity in liquid Na. The black lines are PCFs using the initial 5 ps data and red lines are the averaged PCFs using the data from 5 ps to 30 ps. We can see that there is a negligible difference

between black and red lines, indicating that the geometry was reasonably equilibrated before 5 ps.

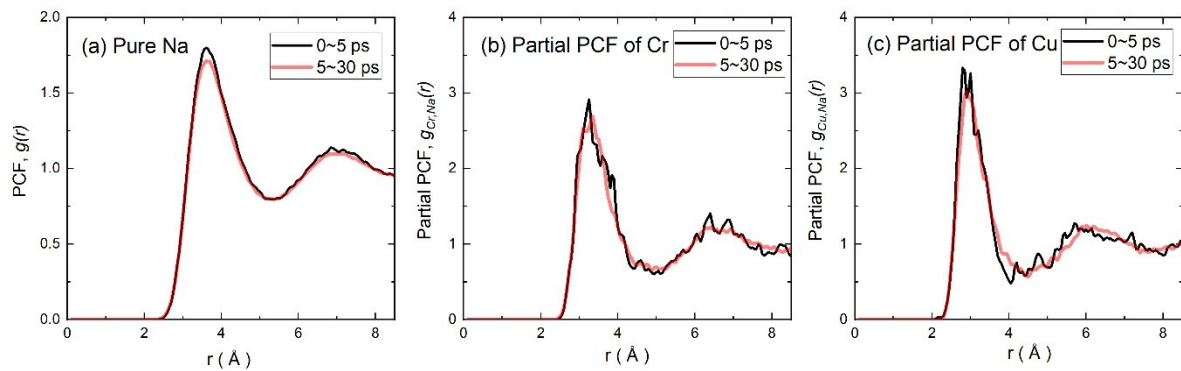


Fig. S2. (a) PCF of liquid Na and partial PCF of (b) Cr impurity and (c) Cu impurity in liquid Na at 1000 K. The black and red lines indicate the PCFs using the initial 5 ps data and data from 5 ps to 30 ps, respectively.