Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary information

Carbon coated face-centered cubic Ru-C nanoalloys

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METHODS: Estimations of pressure and temperature in shock experiments

The dynamic shock experiments of two sets of ball-milled materials, pure Ru and a Ru-C mixture with a molar ratio of 1:2 (Ru: 99.9%, carbon black: 99.9+%), were conducted with a two-stage light gas gun and a chemical detonation system, respectively. The Hugoniot parameters were calculated as following:

1) The Hugoniot parameters of Ru were calculated from known K_0 (bulk modulus at ambient pressure) and K_0' (the first pressure derivative of bulk modulus) of Ru.[1] The shock velocity relationship can be described as $D = C_0 + \lambda U$, where *D* is the shock velocity, *U* is the particle velocity, $C_0 = \sqrt{K_0/\rho_0}$ and $\lambda = (K_0' + 1)/4$ are the Hugoniot parameters.

   $\gamma_0 = 2\lambda - (\frac{a}{2} + \frac{2}{3}$ is the Grüneisen parameter of a material at ambient pressure (For Ru, $a = 2/3$).

   The Hugoniot parameters of carbon were obtained from LANL Shock Hugoniot data:[2] $D = 4.037 + 2.113U$, where C_0 and λ of carbon are 4.037 km/s and 2.113, respectively. The Grüneisen parameter of carbon: $\gamma_0 = 1.10$.

2) The Hugoniot and Grüneisen parameters of dense Ru/C mixture can be calculated from the Hugoniot parameters of Ru and C by the mixture rule:[3]

   $$V_0 = \sum_{i=1}^{n} a_i V_{0i}\ ,\ \frac{V_0}{\gamma_0} = \sum_{i=1}^{n} \frac{a_i V_{0i}}{\gamma_{0i}}\ ,\ \frac{V_0^2}{C_0^2} = \sum_{i=1}^{n} \frac{a_i V_{0i}^2}{C_{0i}^2}\ ,\ \text{and}\ C_V = \sum_{i=1}^{n} a_i C_{vi}\ ,$$

   where a_i , V_{0i} , γ_{0i} , and C_{vi} are the mass fraction, specific volume, Grüneisen parameter, and specific heat at constant volume of *i*th component, respectively. V_0 , C_0, and γ_0 are the specific volume, Hugoniot parameter, and Grüneisen parameter at ambient pressure of dense mixture, respectively.

3) The Hugoniot parameters of porous Ru/C mixture samples can be calculated from the

Hugoniot parameters of dense Ru/C mixture.[4] For a give shock pressure, P_H, the particle velocity of dense material u_p and porous material u can be described as $u^2 = u_p^2 + 2P_H V_0(m-1)/(k+1)$, where m is the porosity of material $m = V_{00}/V_0$, V_{00} is the initial specific volume of porous material, V_0 is the initial specific volume of dense material, $k = 1.4$ is polytropic index of air. According to the shock pressure relationship $P_H = \rho_0 Du$ where D is shock velocity and u is particle velocity, the Hugoniot parameters C_0 and λ of porous material can then be derived from dense material.

4) **The pressure** P_H **,** specific volume V of porous material under shock compression can then be calculated by the impedance match method according to the impact velocity and Hugoniot parameters of flyer, holder, and porous sample.[5]

5) After the shock specific volume V is calculated, **shock temperature** T_H can be calculated by shock temperature of dense material and porosity of sample.[1]

$$T_H = T_0 \exp\frac{-\gamma_0}{V_0}(V_0 - V) + \frac{\rho_0 C_0^2}{C_V}\exp\frac{-\gamma_0}{V_0}(V_0 - V)\int_{V0}^{V}\left[\frac{-\lambda\eta^2}{(1-\lambda\eta)^3}\exp\frac{\gamma_0}{V_0}(V_0 - V)\right]dV + \frac{P_S V_0}{C_V}\frac{m-1}{2 - \frac{\gamma_0 V}{V_0}\left(\frac{m}{1-\eta} - 1\right)},$$

where $\eta = 1 - V/V_0$, T_0 is ambient temperature 300 K, V is the specific volume of shock state, V_0 is the initial specific volume of dense Ru/C mixture, γ_0 is Grüneisen parameter of dense Ru/C mixture at ambient pressure, C_v is specific heat of dense Ru/C mixture, C_0 and λ are Hugoniot parameters of dense Ru/C mixture, m is the porosity, P_S is the pressure of dense Ru/C mixture at volume V. An approximation of $\gamma_0/V_0 = \gamma/V$ is used here.

Reference:

1. F. Jing, *Introduction to Experimental Equation of State*, Science Press, Beijing, 1999.
2. S. P. Marsh, *LANL Shock Hugoniot Data*, University of California Press, Ltd., Berkeley, Los Angeles, London, 1980.

3. M. A. Meyers, *Dynamic Behavior Of Materials*, John Wiley & Son, INC. , New York, Chichester, Brisbane, Toronto, Singapore, 1994.
4. S. S. Batasanov, *Effects of Explosion on Materials: Modification and Synthesis Under High-Pressure Shock Compression*, Springer-Verlag, New York, Berlin, Heidelberg, London, Paris, 1994.
5. A. C. Mitchell and W. J. Nellis, *J. Appl. Phys.*, 1981, **52**, 3363-3374.

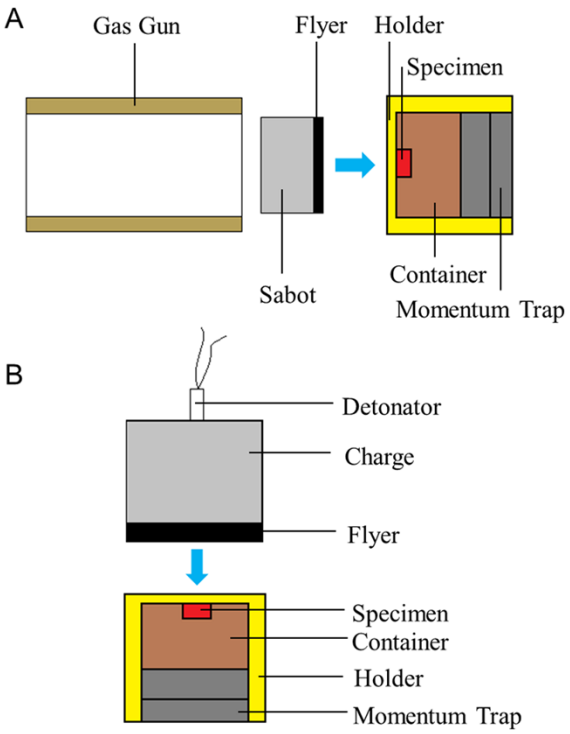

Fig. S1. Schematic diagrams of dynamic shock experimental systems. (a) A light gas gun system. (b) A chemical detonation system. In a light gas gun experiment, the projectile, consisting of copper flyer and sabot, is accelerated to several kilometers per second in the gas gun cannon. Instantaneous high pressure and temperature can be generated when the flyer impacts the container. In a detonation shock experiment, the flyer is accelerated by explosive charge. The sample assembly units are the same in these systems: The sample is contained in a copper capsule. Thick steel disks assembled behind the container serve as momentum trap.

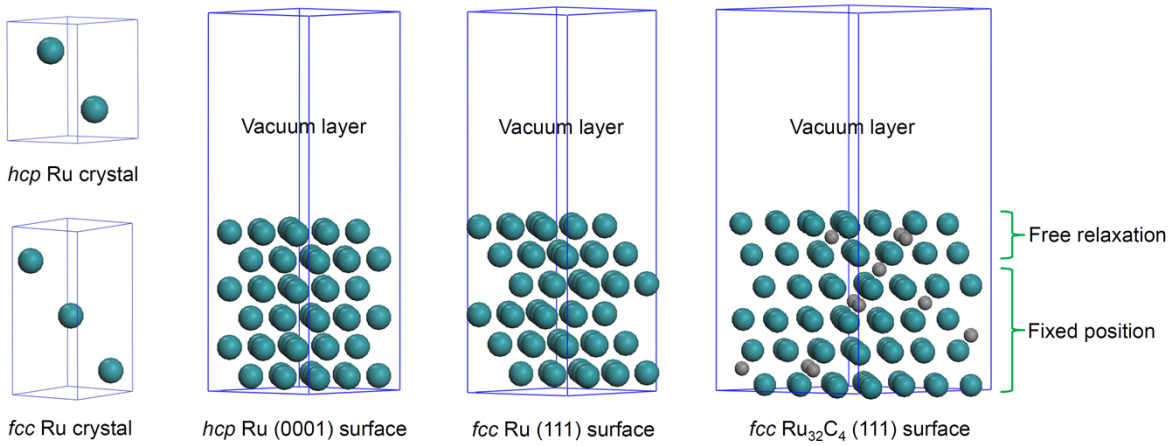

Fig. S2. Bulk crystal and surface models: *hcp* Ru, *fcc* Ru, *hcp* Ru (0001) surface, *fcc* Ru (111) surface, and *fcc* $Ru_{32}C_4$ (111) surface. The illustrated *fcc* Ru crystal structure was rebuilt from the common *fcc* structure by ABC stacking along [111] crystal direction. To build surface models, a vacuum layer of 1.5 nm is added to avoid mirror interaction occurring. The atoms of the top two layers were free to relax in order to simulate the surface state, while the atomic fractional positions of the lower four layers were fixed to maintain the bulk environment.

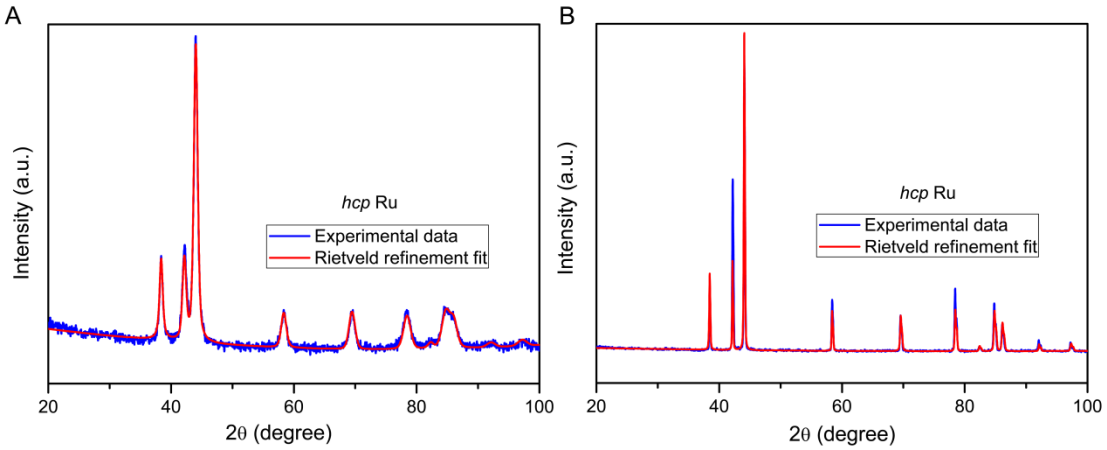

Fig. S3. Ambient-condition XRD patterns of (a) Ball-milled pure Ru powders and (b) Recovered bulk sample after shock impact (Cu K_α: λ=1.5418 Å). Blue and red lines are experimental data and Rietveld refinement fit, respectively.

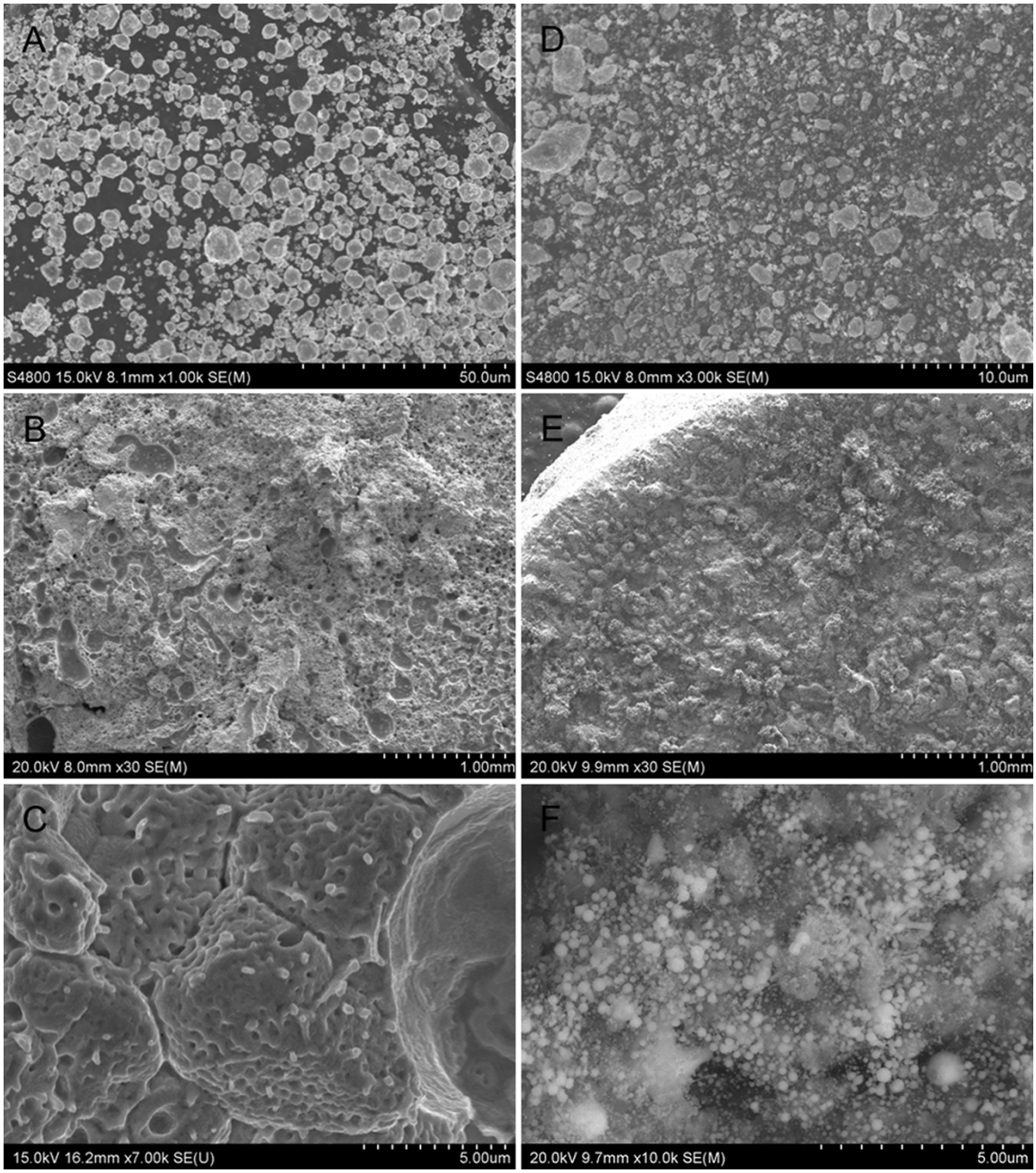

Fig. S4. SEM images of pure Ru and Ru-C mixture before and after the dynamic shock experiments. (a) Ball-milled pure Ru powders. (b) and (c) Shock-recovered Ru bulk sample. (d) Ball-milled Ru-C mixture powders. (e) and (f) Shock-recovered Ru-C mixture bulk sample.

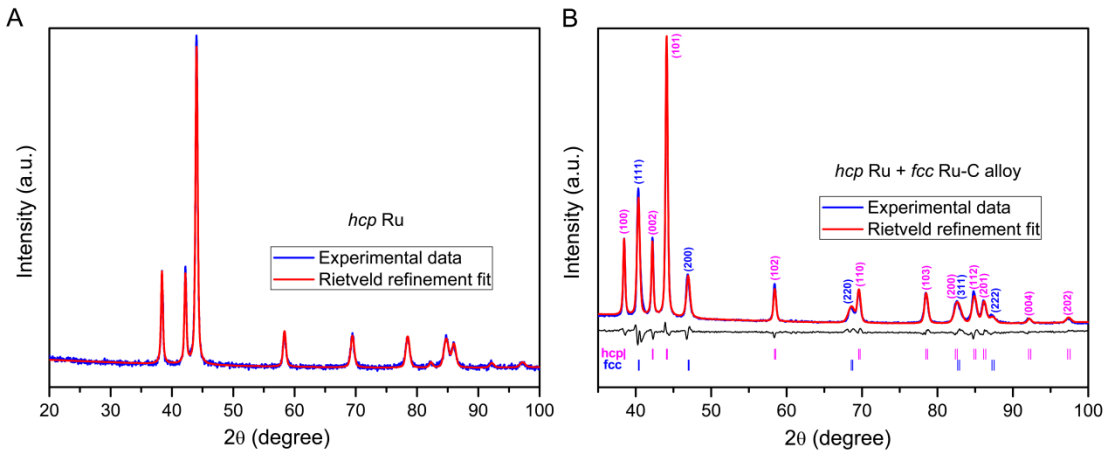

Fig. S5. Ambient-condition XRD patterns of (a) Ball-milled Ru-C mixture powders and (b) Shock-recovered Ru-C mixture (ground powders) (Cu K_α: λ=1.5418 Å). Blue line, red line, and vertical tags are experimental data, Rietveld refinement fit, and calculated Bragg positions of corresponding structures, respectively.

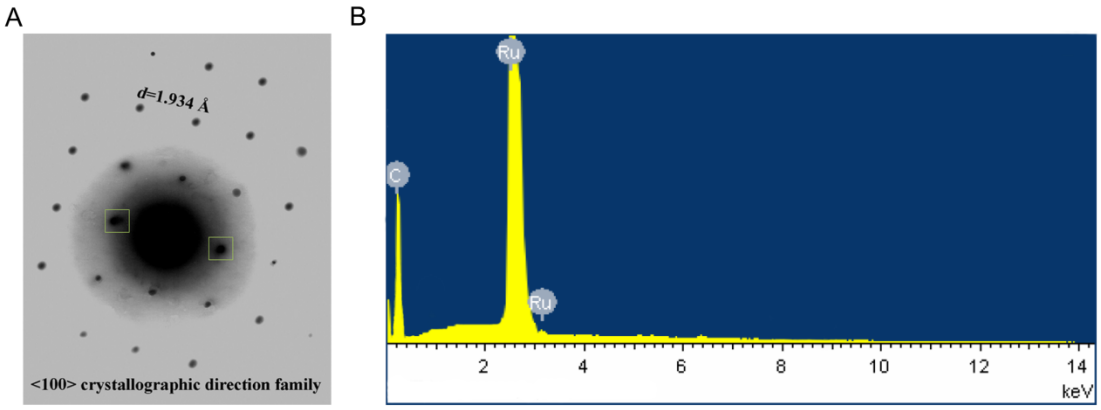

Fig. S6. (a) Selected area electron diffraction and (b) Energy dispersive spectroscopy (EDS) of *fcc* Ru-C nanoalloy. The marked diffraction spots emphasize the lattice distortion due to carbon dissolution. The EDS was obtained from carbon-coated Ru-C nanoalloy.

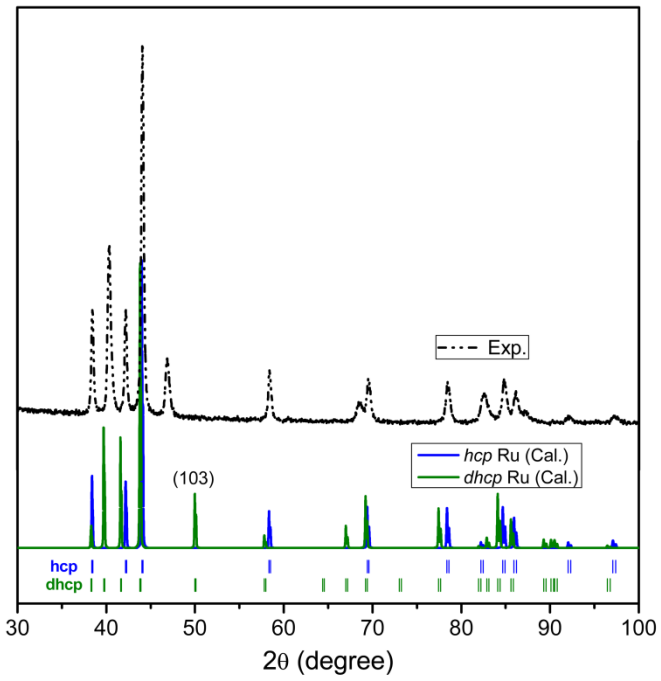

Fig. S7. Comparison of experimental XRD of shock-recovered Ru-C mixture (black dots) and simulated XRD from *hcp* Ru (blue line) and *dhcp* Ru (green line).

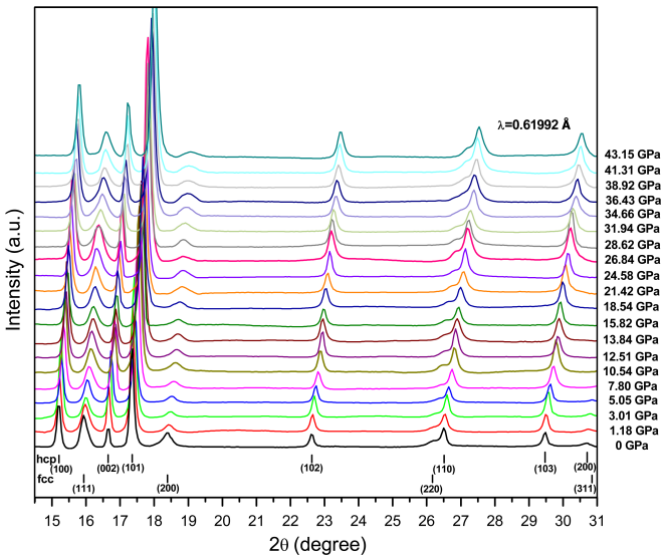

Fig. S8. Room temperature synchrotron XRD patterns of shock-recovered Ru-C mixture (ground powders) under various pressures. The photon wavelength is 0.61992 Å.

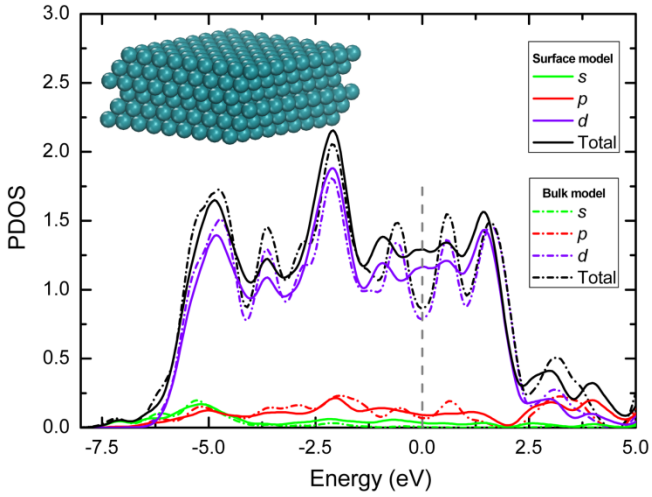

Fig. S9. Density of states (electrons per eV per Ru atom) of hypothetical *fcc* Ru bulk and surface models. Surface model of *fcc* Ru(111) is shown as the inset.

Table S1. Calculated Mulliken populations, Hirshfeld charges, and bond lengths in bulk and surface of *hcp* Ru, *fcc* Ru and *fcc* Ru-C alloy. The used covalent electrons for atomic calculation are Ru $4s^2 4p^6 4d^7 5s^1$ and C $2s^2 2p^2$.

Phase	Mulliken Populations (*e*)					Hirshfeld Charge (*e*)	Ru-Ru bond length (Å)	Ru-C bond length (Å)
	Atom	*s*	*p*	*d*	Total			
hcp Ru bulk	Ru	2.30	6.80	6.89	16.00	0	2.657 2.721	
hcp Ru (0001) surface	Ru	2.31 2.66 2.30	6.65 6.55 6.80	6.88 6.96 6.90	15.84 16.17 15.99	0.01 -0.01 0	2.583 2.664 2.657 2.721	
fcc Ru bulk	Ru	2.33	6.77	6.90	16.00	0	2.693	
fcc Ru (111) surface	Ru	2.32 2.67 2.32	6.64 6.52 6.76	6.88 6.97 6.91	15.85 16.16 15.99	0.01 -0.01 0	2.608 2.709 2.693	
fcc Ru-C alloy bulk	C	1.44 1.41	3.17 3.16	0 0	4.62 4.57	-0.35 -0.33		1.947 1.956 2.047
	Ru	2.32 2.34 2.30 2.25	6.70 6.79 6.75 6.64	6.90 6.88 6.90 6.93	15.92 16.02 15.94 15.82	0.01 0 0.05 0.11	2.624 2.647 2.685 2.766 2.825 2.837 2.850 2.895	
fcc Ru-C alloy (111) surface	C	1.44 1.43 1.41 1.41	3.17 3.16 3.11 3.15	0 0 0 0	4.61 4.59 4.52 4.56	-0.35 -0.34 -0.31 -0.33		1.921 1.948 1.951 2.038 2.048 2.064
	Ru	2.30 2.30 2.60 2.33 2.32 2.64 2.62 2.33 2.65 2.34 2.25	6.62 6.73 6.46 6.66 6.68 6.48 6.53 6.63 6.52 6.78 6.57	6.89 6.90 6.97 6.89 6.92 6.97 6.97 6.89 6.97 6.89 6.92	15.81 15.93 16.04 15.88 15.91 16.09 16.12 15.84 16.14 16.00 15.73	0.06 0.04 0.04 0.02 0.01 -0.01 -0.02 0.03 -0.02 0 0.11	2.497 2.528 2.548 2.610 2.617 2.630 2.637 2.649 2.656 2.687 2.763 2.795 2.827 2.840 2.853 2.897 2.989	