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Supporting information for article:

Hardening tungsten carbide by alloying elements with high work function

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The influences of the alloying elements on electron density may be explained by the local potential distribution analysis. Fig.S1 illustrates the local potential distribution in (0001) W-terminated plane and $(11\bar{2}0)$ plane of WC doped with Nb and Re. As demonstrated in Fig.S1, the local potentials between adjacent Nb-W and Nb-C are higher than those between adjacent W-W and W-C, which corresponds to the lower electron densities around Nb atoms than those around W atoms since electrons tend to redistribute to low potential regions. However, the local potentials between adjacent Re-W and Re-C are lower than those between adjacent W-W and W-C. This is an indication that alloying WC with elements with high work functions may increase the electron density and strengthen the atomic interactions.

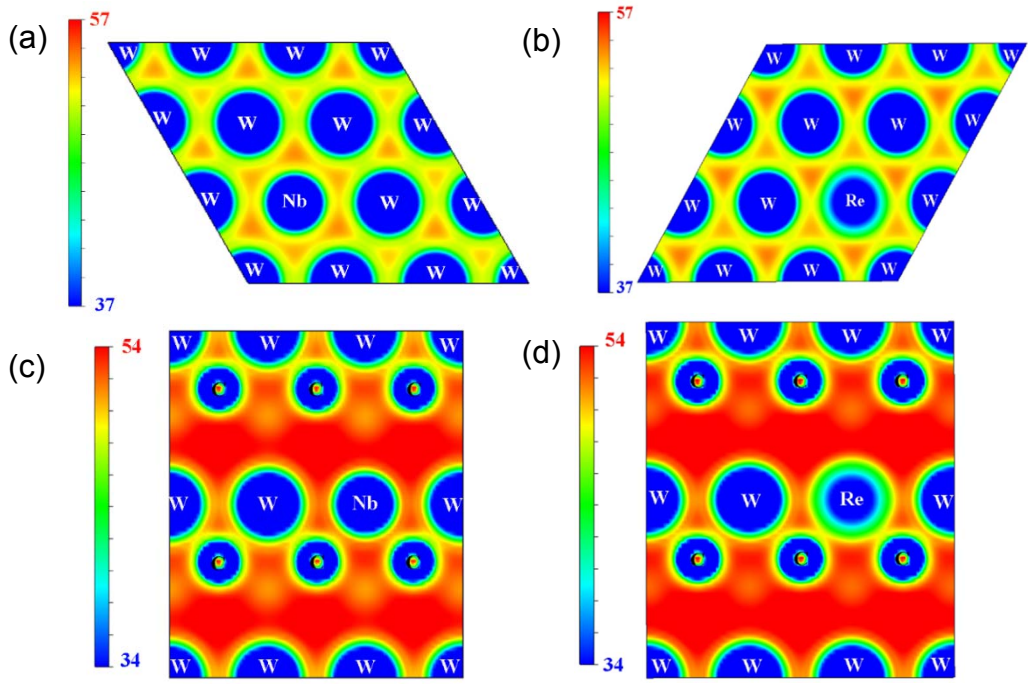

Figure S1 Local potentials (eV) in (0001) W-terminated plane of (a) Nb and (b) Re doped WC, and local potentials (eV) in $(11\bar{2}0)$ plane of (c) Nb and (d) Re doped WC. Red regions have higher potentials than green and blue regions.

The effects of alloying elements on work function and mechanical properties of WC may be also reflected by electron localization function (ELF). ELF is a dimensionless index in the range of 0 to 1, that expresses the electron localization with respect to the uniform electron gas (Becke & Edgecombe, 1990, Savin et al., 1997). In the homogeneous free electron gas, ELF has the value of 0.5 everywhere. The value of 1 corresponds to the prefect localization, and the value of 0 refers to delocalization or very low electron density. As illustrated in Figs.S2 (a) and (b), the ELFs have high values between carbon and metal atoms, which corresponds to the covalent bonds between metal and carbon atoms. However, the values between metal-metal atoms are relatively low, which indicates the metallic bonds between metal atoms. The ELF values near carbon atoms are much higher than those near metal atoms, which means that electrons are more localized around carbon atoms and indicates the formation of partial ionic bonds. The formation of ionic bonds is also reflected by the bonding charge density. The bonding charge density was obtained from the charge density difference between the valence charge density of the bulk crystal and the superposition of the valence charge density of the neutral constituent atoms. As shown in Figs.S2 (c) and (d), a larger amount of charge transfers from Re to C than from W to C, however the amount of charge transfer from Nb to C is smaller. This indicates the formation of stronger ionic bonds between Re and C than between W and C, and weaker ionic bonds between Nb and C. The chemical bonding analysis based on ELF and bonding charge density is consistent with the information gotten from DOS in Fig.1. If look at closer to the ELF between carbon atom and metal atom, one may see that the ELF value between Re and C is larger than that between W and C, however, the value between Nb and C is smaller than that between W and C. It indicates Re may strengthen the covalent bond and Nb may weaken that in WC. A higher degree of electron localization in Re doped WC also renders electrons harder to escape, corresponding to a higher work function.

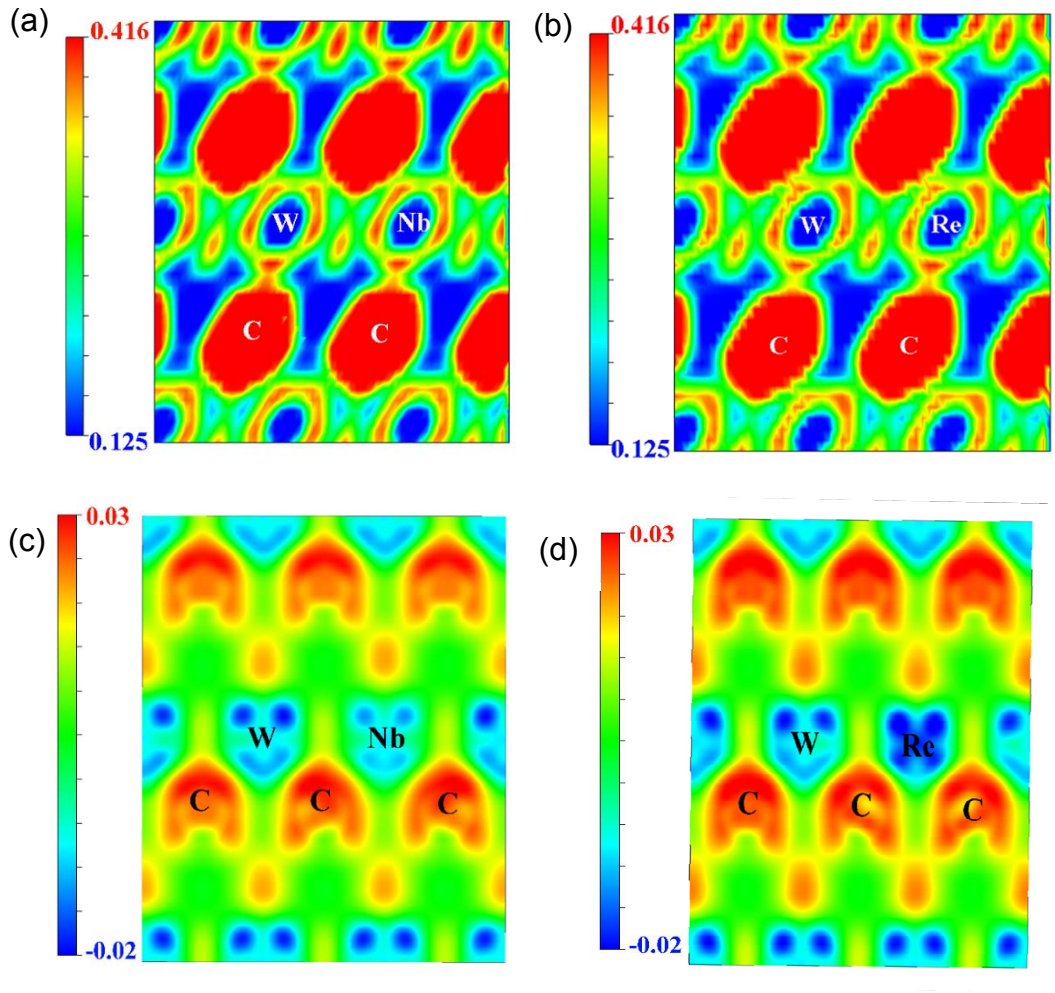

Figure S2 (a)(b) Electron localization function (ELF) of Nb and Re doped WC $(11\bar{2}0)$ plane. Electrons in red and yellow regions are more localized than those in green and blue regions. (c)(d) Bonding charge density (bohr-3) of Nb and Re doped WC $(11\bar{2}0)$plane. Red and blue indicate the electron accumulation and depletion, respectively.

References

Becke, A. D. & Edgecombe, K. E. (1990). *The Journal of Chemical Physics* **92**, 5397-5403.