The application of aluminothermic reduction to metal/alloy production from oxides – a review

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1. Introduction

Metal extraction and processing sectors are challenged to meet the high demand for metals while maintaining the effectiveness and sustainability of existing processes. Various reductants can be used to extract metals from their oxides.

The use of aluminium (Al) as a reductant, called aluminothermic reduction, has been applied in a number of applications to reduce certain oxides.

Figure 1 provides the ΔG and ΔH from the reduction reactions of oxides by Al. It shows that the reduction of Cu_2O is highly spontaneous over the range temperature of 0-2000 °C followed by NiO, CoO, Fe_2O_3, Cr_2O_3, MnO and TiO_2.

In comparison, the reduction of Li_2O by Al is not thermodynamically spontaneous at temperatures lower than 1240°C. However, applying low pressures, i.e. 10^{-5} atm, would lower the minimum temperature of Li_2O reduction to 580 °C.

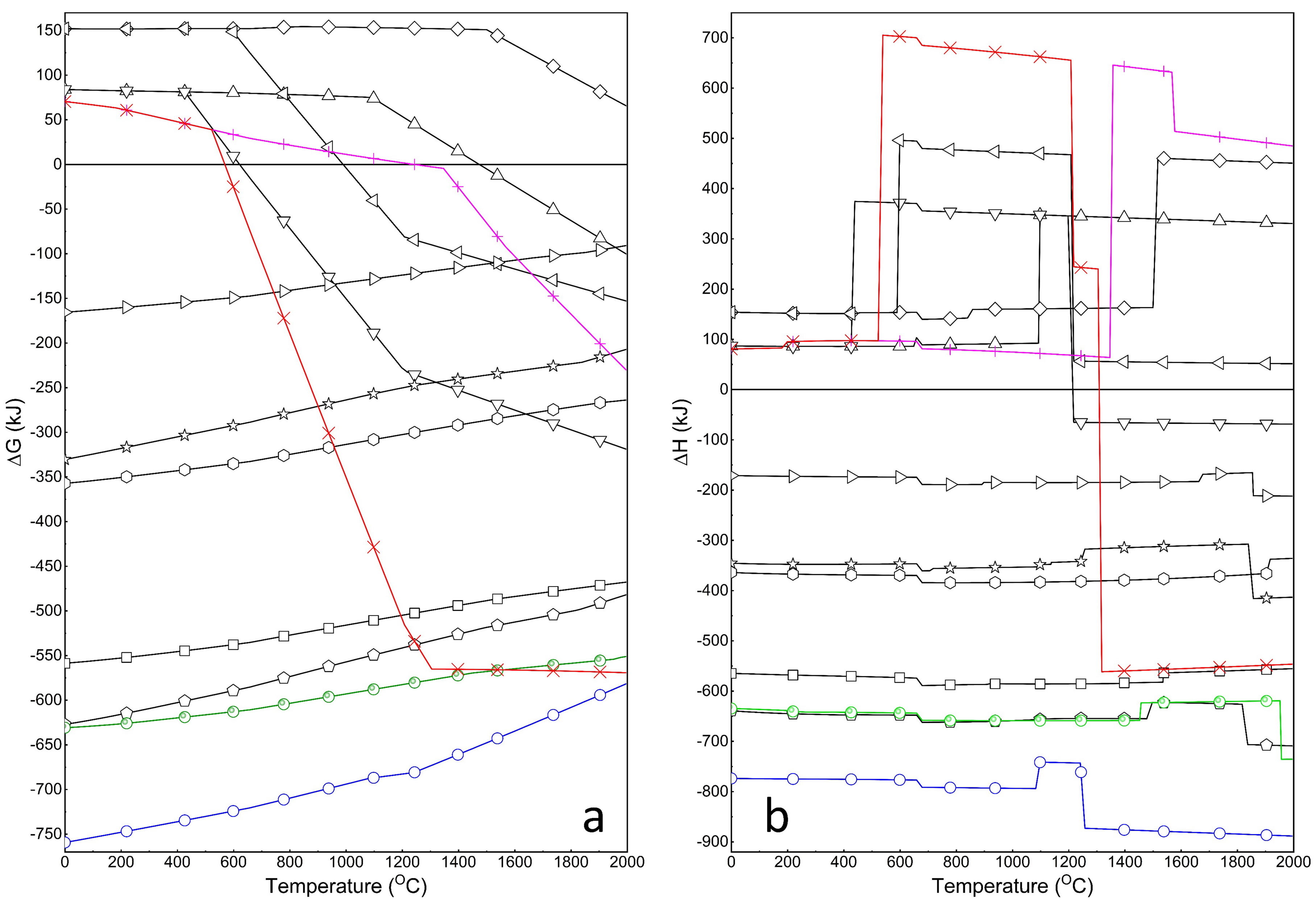

Figure 1: The (a) ΔG° and (b) ΔH° data of some oxides reduction by Al..

- $^4/_3$ Al + $^2/_3$ Fe_2O_3 = $^4/_3$ Fe + $^2/_3$ Al_2O_3
- $^4/_3$ Al + 2 Cu_2O = 4 Cu + $^2/_3$ Al_2O_3
- $^4/_3$ Al + 2 MgO = 2 Mg + $^2/_3$ Al_2O_3 (1 atm)
- $^4/_3$ Al + 2 MgO = 2 Mg + $^2/_3$ Al_2O_3 (10^{-5} atm)
- $^4/_3$ Al + 2 CaO = 2 Ca + $^2/_3$ Al_2O_3 (1 atm)
- $^4/_3$ Al + 2 CaO = 2 Ca + $^2/_3$ Al_2O_3 (10^{-5} atm)
- $^4/_3$ Al + TiO_2 = Ti + $^2/_3$ Al_2O_3
- $^4/_3$ Al + $^2/_3$ Cr_2O_3 = $^4/_3$ Cr + $^2/_3$ Al_2O_3
- $^4/_3$ Al + 2 MnO = 2 Mn + $^2/_3$ Al_2O_3
- $^4/_3$ Al + 2 CoO = 2 Co + $^2/_3$ Al_2O_3
- $^4/_3$ Al + 2 NiO = 2 Ni + $^2/_3$ Al_2O_3
- $^4/_3$ Al + 2 Li_2O = 4 Li + $^2/_3$ Al_2O_3 (1 atm)
- $^4/_3$ Al + 2 Li_2O = 4 Li + $^2/_3$ Al_2O_3 (10^{-5} atm)

2. Ignition of thermite reaction

The thermite reaction is used to describe any exothermic reactions involving reduction-oxidation of metallic oxides, M_xO_y, with metal N to form N_xO_y and metallic M.

The occurrence of the adiabatic state is common in some thermite systems (including aluminothermic). The enthalpy produced by the reaction is released and increase the temperature of the system, T_{ad}.

Figure 2 illustrates the adiabatic state of aluminothermic reduction of Fe_2O_3 from a thermodynamic perspective where the ΔH° is released to form liquid Al_2O_3, liquid Fe, and a small amount of gas Fe.

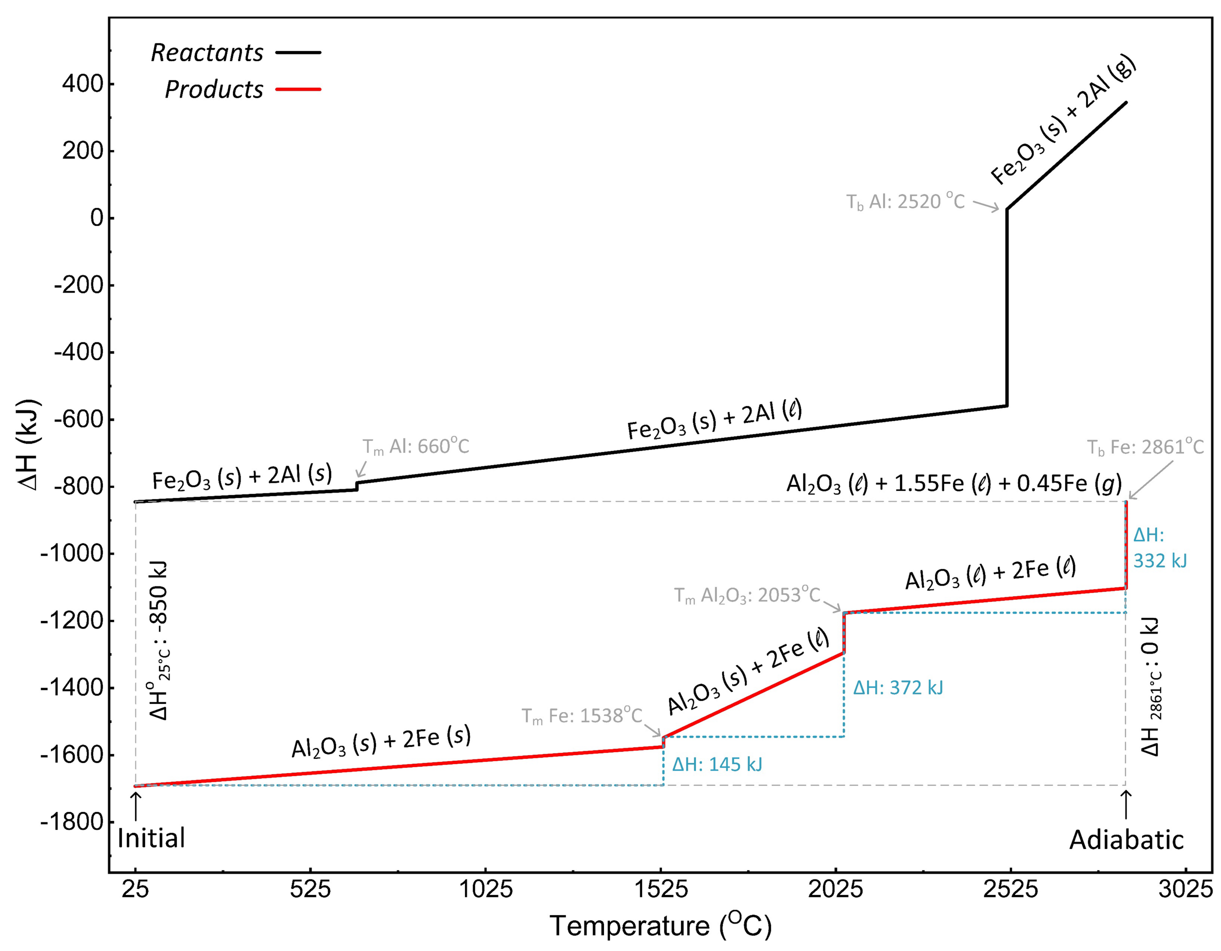

Figure 2: Adiabatic illustration of the aluminothermic reduction of Fe_2O_3.

When the enthalpy from the reaction is released, one of the manifestations is the occurrence of ignition (i.e. the thermite reaction).

As an example, Nababan *et al.* [1] reported that the reaction between Al and pure $LiCoO_2$ as shown in Figure 3 would be transformed into the smelting stage producing liquid slag, liquid CoAl alloy, and Li gas.

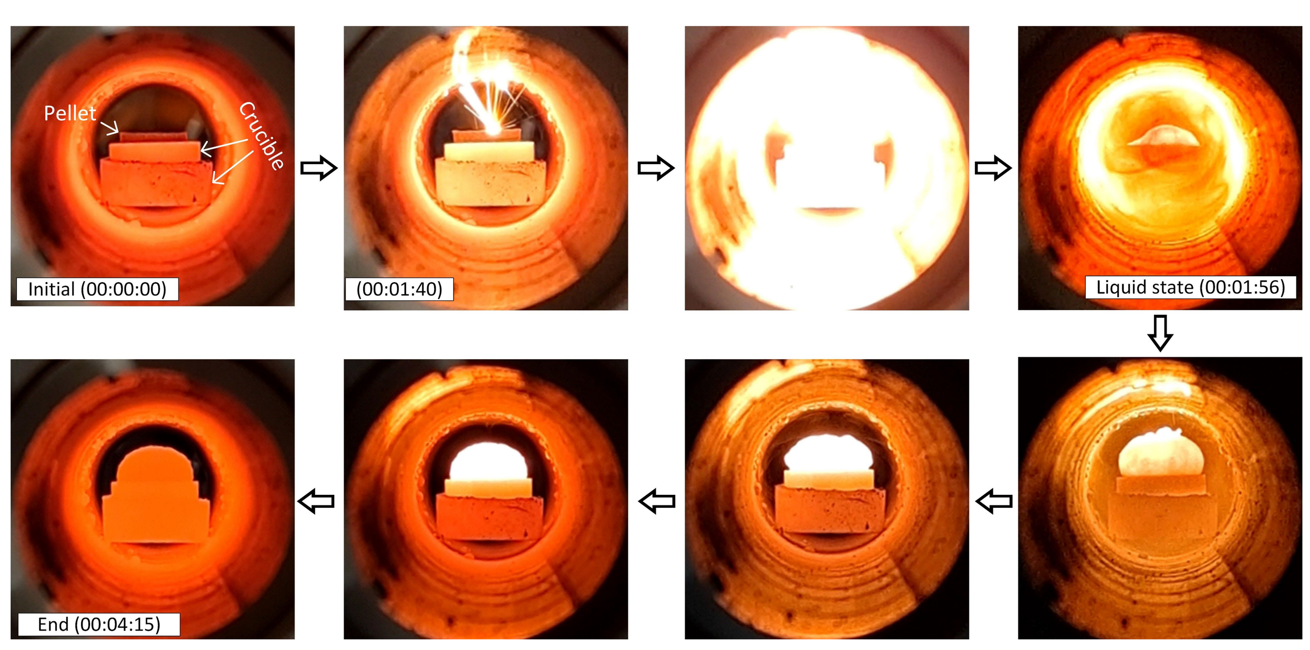

Figure 3: Macroscopic observation of the aluminothermic reduction of $LiCoO_2$ at the initial temperature of 850°C showing an ignition of the thermite reaction and melting of the sample [1].

3. Discussion

A study by Nababan *et al.* [2] found that the amount of Al (composition of the sample), the sample weight and size, and the initial heating temperature affect the occurrence of spontaneous ignition of the thermite reaction in the $LiCoO_2$ aluminothermic reduction system leading to the partial/full melting of the sample.

In some systems, although the reaction between Al and the oxide occurs, the ignition of the thermite reaction leading to a full smelting does not always spontaneously follow.

4. Future outlook

The aluminothermic reduction has the potential to be a common route to produce various metals/alloys. This route has received attention considering the current emphasis on low-carbon processes particularly if the reduced metals are of higher value. Aluminothermic can also be applied to the recovery of valuable metals from secondary resources e.g. slag, tailing, and other wastes.

One of the challenges in aluminothermic reduction is the high energy input required to produce the Al from its common ore, bauxite. However, it is possible that the secondary Al could potentially be used as an alternative.

Xu *et al.* [3] studied a carbon-free smelting reduction process to recover valuable metals from waste copper slag using secondary Al dross as a reductant. Figure 4 shows photographs of the slags and iron ingots after reduction under different basicity (CaO/SiO_2 mass ratio) values, R.

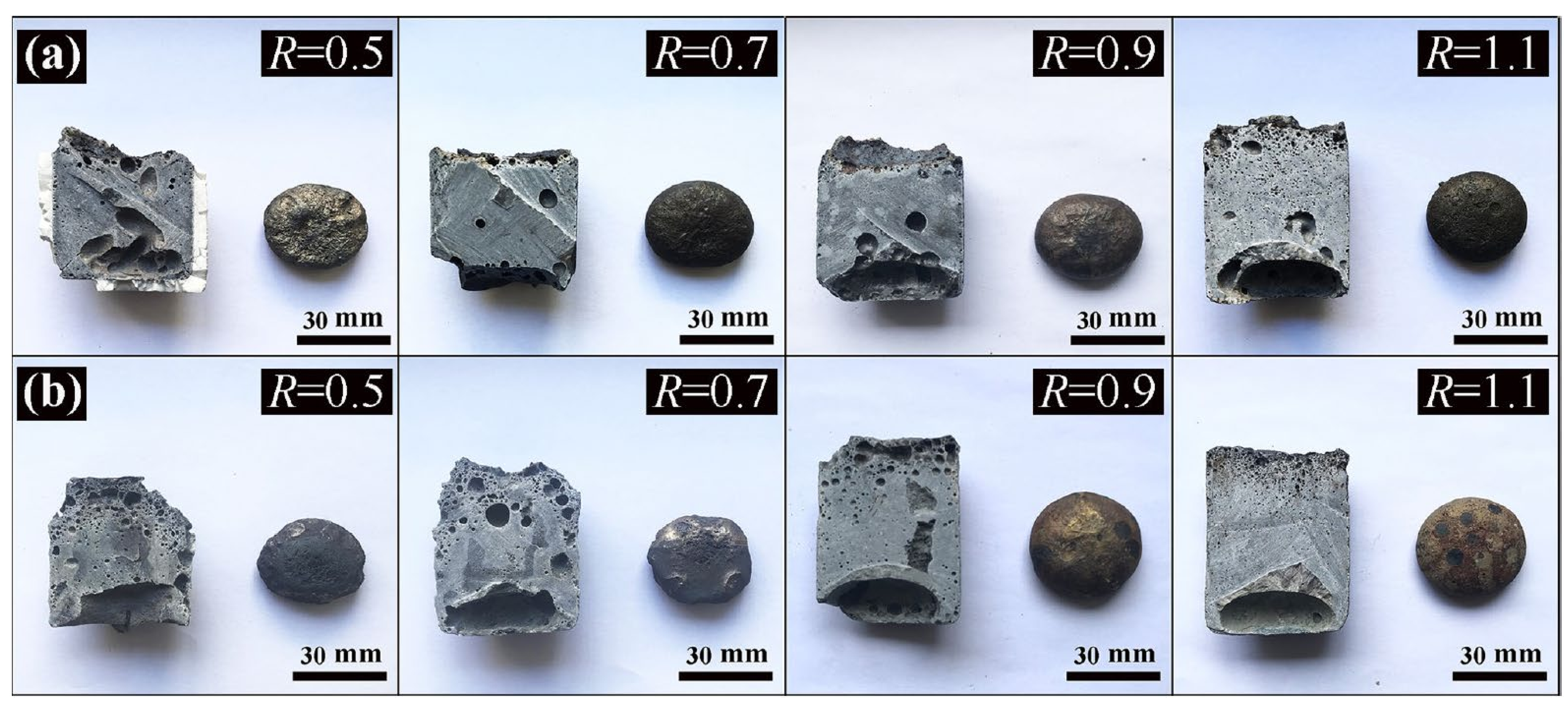

Figure 4: Photographs of the secondary slags and the separated ingots after reduction under different basicity values: (a) 1500°C, (b) 1600°C [3]

Another challenge that a typical aluminothermic process has is that some Al would be solved into a liquid alloy to form an intermetallic phase which may be not desired. This will require further processes to purify the produced metal.

5. Conclusion

- This review has provided a summary of the basic reaction system involving aluminothermic reduction of oxides.
- The occurrence of ignition in an aluminothermic system is determined by various parameters.
- Aluminothermic reduction could be utilized to recover valuable metals from secondary resources.

6. References

1. D. Nababan, R. Mukhlis, Y. Durandet, L. Prentice, M. Rhamdhani, Separation of Li and Co from $LiCoO_2$ Cathode Material Through Aluminothermic Reduction: Thermodynamic Calculations and Experimental Results, Metallurgical and Materials Transactions B, 2024.
2. D. Nababan, R. Mukhlis, Y. Durandet, L. Prentice, M. Rhamdhani, Separation of Li and Co From LiCoO2 Cathode Material Through Aluminothermic Reduction: Investigation of the Thermite Reaction, Metallurgical and Materials Transactions B, 2024.
3. L. Xu, Y. Liu, M. Chen, N. Wang, Efficient recycling of valuable metals from waste copper slag by using secondary aluminium dross as a novel reductant, Metallurgical and Materials Transactions B, 2022.

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