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The assessment of growth kinetics in the intermetallic layers of Al-Al_xNi_y-Ni laminate composites

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Abstract. Ni aluminides have technologically attracted much attention as oxidation protective layers on Ni-superalloys for high-temperature and harsh environments applications as well as for reinforcements in metal-matrix composites. Among the Ni aluminides, the AlNi compound exhibits the best combination of oxidation-protective characteristics and hardness; thus there is a progressive demand to produce it particularly through convenient in-situ fabrication processes. Therefore, the evaluation of growth kinetics in Al_xNi_y layers is of crucial importance in determining an optimum compound formation process. To this purpose, Al-Ni intermetallic laminate composites were produced through cold roll bonding and subsequent annealing of aluminum and nickel sheets. The microstructure of the intermetallic layers was investigated in order to specify the controlling mechanisms and subsequently the growth model of the different phases. The Al_3Ni layer was kinetically the first to appear but started to decompose at the expense of the AlNi compound when the direct source of Al disappeared for the reactive diffusion couples. The Al_3Ni layer growth was initially controlled by bulk diffusion, but then at $T \geq 525°C$ was modified as a function of competition between formation and consumption, whereas the AlNi growth was governed strongly by the interfacial reaction. The time dependence of the growth rate revealed different behaviors of linear and parabolic kinetics. The overall assessment revealed a bulk diffusion-controlled growth for all of the intermetallic layers. Arrhenius parameters could be derived for the Al_3Ni layer, while it was impossible for the AlNi phase because the formation of this layer was caused by a mixture of diffusion mechanism.

1. Introduction

Between nickel aluminides, the AlNi intermetallic phase exhibits the best combination of oxidation-protective characteristics and hardness, which provokes a great interest in Al-AlNi-Ni composites. Metal-intermetallic laminates (MIL) composites have the potential to combine various functions, which may be of use for high-temperature structural applications such as heat exchangers, which require appropriate thermal management [1,2].

There are some inconsistencies in the data on the growth kinetics of intermetallic phases. For instance, according to Michaelsen and Barmak [3] the growth of Al_3Ni phase indicates a parabolic dependence on the annealing time, whereas Jung et al [4] have reported that the growth kinetics of Al_3Ni phase does not obey the parabolic law. Moreover, researchers have reported conflicting results on Al and Ni asymmetric interdiffusion coefficient. Hence, the dominant diffusing element during the

formation of intermetallic phases is still entirely unclear under similar process conditions [2,5–7]. However, Al_3Ni phase was recognized as the first kinetically favored intermetallic phase, independently of the concentration gradient [5] and imposed strain level [8].

Therefore, a more detailed examination of the formation mechanism of intermetallic phases is of crucial importance to better control the processing of these materials and the aim of this work is to investigate the formation mechanisms and growth kinetics of intermetallic phases in the Al-Ni diffusion couple fabricated by the roll bonding process.

2. Experimental procedure

Commercially pure aluminum and nickel were used as initial materials in sheet form. An Al-Ni-Al sandwich was subjected to cold roll bonding (CRB) by 90% reduction in thickness. The details of materials and CRB process were given elsewhere [8]. In order to form Al_xNi_y intermetallic compounds, the cold roll bonded composite with the dimensions of $200 \times 60 \times 0.5\ mm^3$ was annealed in the temperature range of 300 to 640 °C for 1 and 4 hours.

In addition to a conventional optical microscopy (OM, Olympus) the microstructural evolution was monitored with a field emission gun scanning electron microscope (FEG-SEM Quanta-450®, FEI) equipped with EBSD facility of type TSL-EDAX® and an energy dispersive spectrometer (EDS).

The microstructure of Al/Ni interface was identified by observing sites of size (100-400 µm) × (30-150 µm). Kikuchi band indexing in EBSD were acquired with OIM™ software and gathered at an accelerating voltage of 20 kV, a working distance of 14 to 16 mm with step sizes in the range of 50 to 80 nm. Samples were tilted 70˚ for acquiring the maximum yield of backscattered electrons. The thickness of the continuous or segmented layers of the intermetallic phases was determined at several points of the formed layers using image analysis software (ImageJ2)

3. Results and discussion

Figure 1 shows BSE images of intermetallic laminate composites obtained through annealing. The intermetallic layer(s) was formed along the Al/Ni original interface, visibly present except for the samples annealed at 300°C. Figure 2a and b shows the dimensions of the intermetallic layers as a function of temperature. The layers are mainly composed of Al_3Ni and AlNi compounds according to the phase analysis results listed in Table 1. This table also reveals that other compounds possess relatively negligible thickness.

Table 1. Various phase zones which were detected across Al-Ni interface in TD plane of samples using EDS and Kikuchi band indexing in EBSD.

Zone	Average of Spectrums in EDS		Probable phases	Indexed results in EBSD with confidence index (CI)	Confirmed phases	Ave. thickness of reacted zones (µm)
	Al at.%	Ni at.%				
(A)	1.3	98.7	Nickel	well-indexed nickel, CI=0.8	Nickel	Base metal
(B)	17	83	Diffusion zone	well-indexed (Ni), CI= 0.8	Ni-riched solid solution	~0.5
(C)	30.1	69.9	$AlNi_3$ or ($AlNi_3$+Al_3Ni_5)	well-indexed $AlNi_3$, CI=0.75 not indexed Al_3Ni_5, CI=0.03	$AlNi_3$	~0.5
(D)	55.3	44.7	(Al_3Ni_2+AlNi) or Al_3Ni_2	indexed grains as AlNi, CI= 0.3 indexed grains as $AlNi_3$, CI= 0.41 not indexed Al_3Ni_2, CI=0.01	Mixture of $AlNi_3$+AlNi	Various (0-1.6)
(E)	48.3	51.7	AlNi	well-indexed, CI= 0.49	AlNi	Various (0-20)
(F)	76.8	23.2	Al_3Ni	well-indexed, CI= 0.3	Al_3Ni	Various (0-9)
(G)	100	0	Al	well-indexed nickel, CI=0.7	Aluminum	Base metal

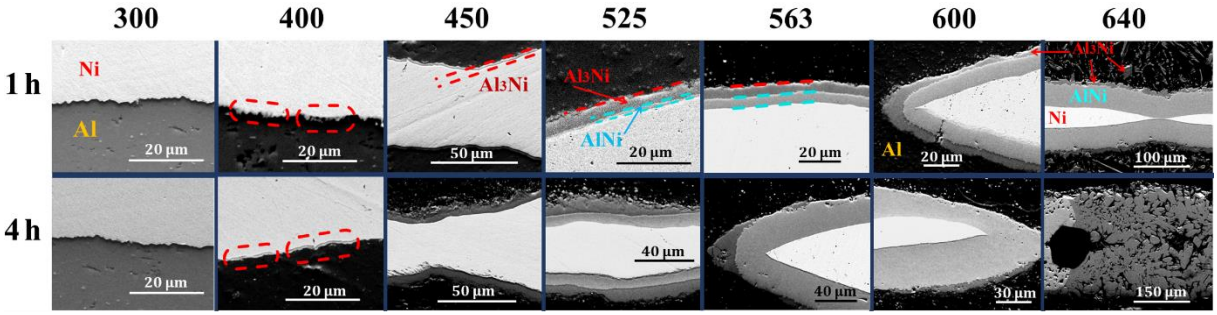


Figure 1. BSE-SEM images of interfaces on TD section of CRB-processed composites after annealing at various times and temperatures.

As shown in Figure 1, the Al phase was melted at 640°C and the interface reactions were no longer solid state. Hence, this temperature data are not given in next results.

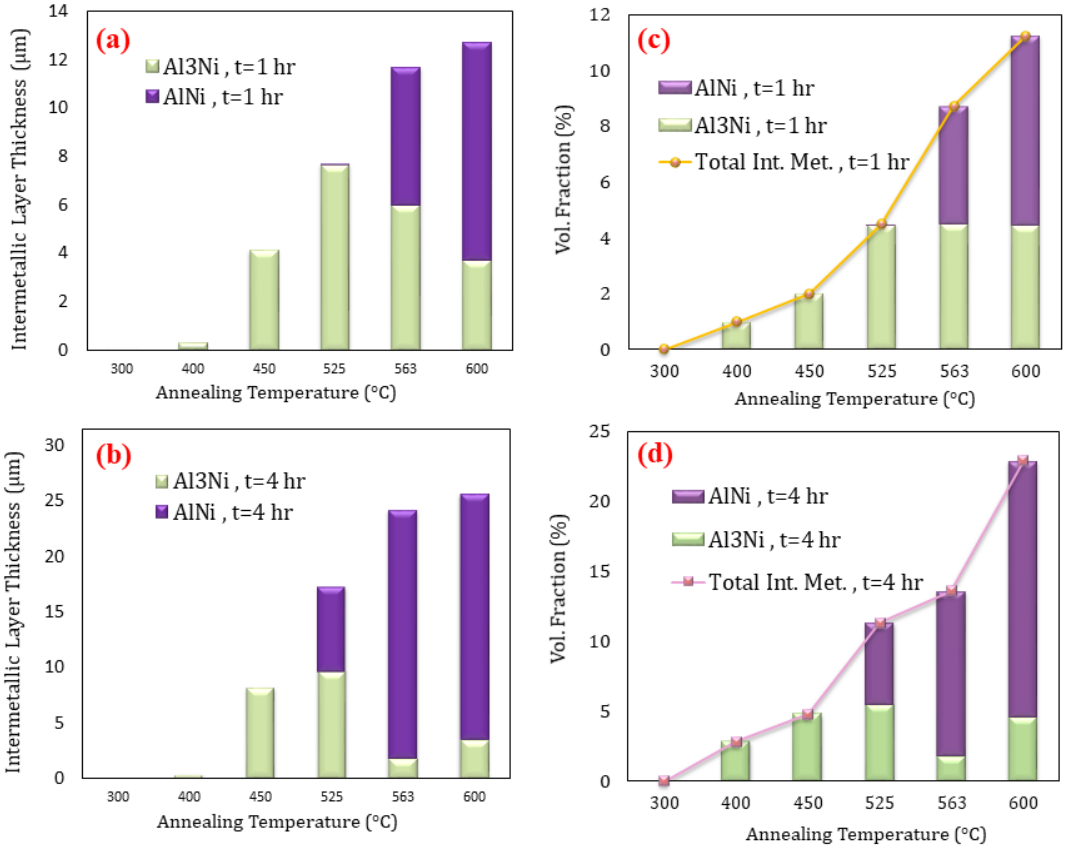


Figure 2. Intermetallic layer thickness/volume fraction vs. temperature during 1 h (a, c) and 4 h (b, d) annealing.

Based on the general empirical equation (1) proposed by Kidson [9], it is possible to model the growth of the thickness of a layer:

$$W_i = kt^n \quad (1)$$

$$ln(W)_i = n\,.\,ln(t) + ln(k) \quad (2)$$

whereby W_i represents the thickness of layer i; k= the growth rate constant; t= time [min] and n= kinetics exponent. From a double logarithmic plot, n and k values can be derived from a linear fit of the

experimental data (cf. Figure 3). However, the accuracy of the results (cf. Table 2) may be influenced by the only two values of the time.

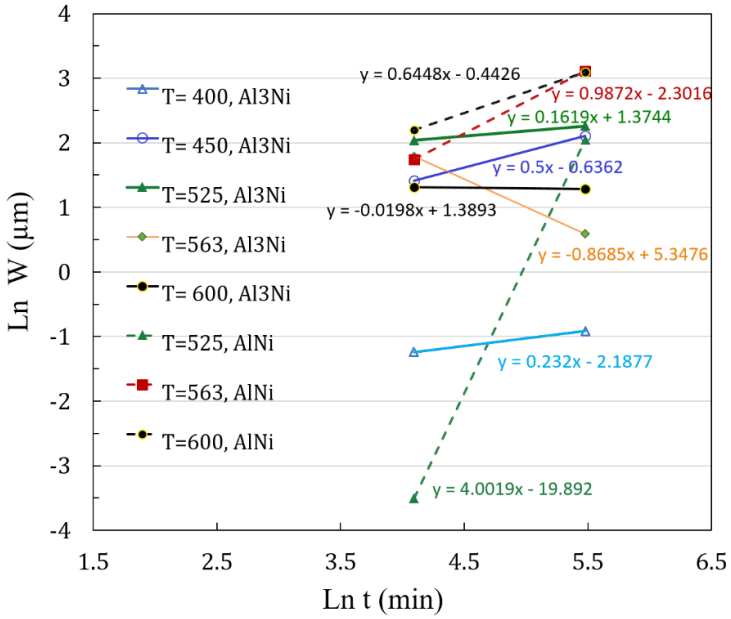


Figure 3. LnW_i versus Lnt for Al_3Ni and AlNi compounds.

Table 2. Growth kinetics parameters of n and k in Al_3Ni and AlNi layers.

Kinetics parameters \ *T(°C)*		**400**	**450**	**525**	**563**	**600**
n	Al_3Ni	0.38	0.5	0.16	-0.81	-0.02
	AlNi	-	-	4.00	0.99	0.65
Ln k	Al_3Ni	-2.19	-0.64	1.37	5.35	1.39
	AlNi	-	-	-19.89	-2.30	-0.44
k	Al_3Ni	0.12	0.53	3.95	180.10	4.01
	AlNi	-	-	2.30	1.00	0.64

The factor n is associated with the controlling mechanism of the intermetallic layer growth process. In terms of quantitative assessment, n=1 demonstrates interfacial reaction controlled growth; n=0.5: bulk diffusion controlled growth and n=0 corresponds to a balance between the layer formation and decomposition during a secondary reaction.

Intermetallic layers may exhibit different behaviors, i.e. sequential growth, concurrent growth and layer shrinkage through decomposition. The last one was observed from 563°C onward, owing to the fact that Al_3Ni (i.e. the Ni-poorest intermetallic) had already started to be consumed at expense of the AlNi compound when the Al direct source disappears from the reactive diffusion couples. Up to 450°C, only Al_3Ni layer was formed and afterwards followed the second stage of a two-stage growth process. The parabolic growth kinetics suggests bulk diffusion controlled growth until the growth kinetics is disturbed by the emerging new AlNi phase at $T \geq 525$°C (the volume fraction of intermetallic layers readily indicates a change in the trend due to this disturbance, cf. Figures 2 c, d). Indeed, a part of the Al_3Ni layer is consumed through the reaction at the Al_3Ni/Ni interface, cf. Equation 3. Eventually, the growth rate is a function of the competition between Al_3Ni direct formation by diffusion and consumption by the interfacial reaction, while the new phase (AlNi) growth is strongly controlled by the interfacial reaction.

$$Al_3Ni + 2Ni \rightarrow 3AlNi \quad (3)$$

Afterwards, increasing the temperature by only ~40° (T=563°C) results in a further increase of the relative thickness/fraction of the AlNi layer. In this stage, AlNi growth kinetics is linear, still controlled by the reaction (equation 3) at Al_3Ni/AlNi interface, but not as strong as that of at the lower temperature (525°C). In the meanwhile, the Al_3Ni decomposition rate prevailed the formation rate at the Al/Al_3Ni interface. After that, increasing the temperature close to the melting point of Al, the atomic mobility is promoted accelerating bulk diffusion. On the one hand, it results in a balance between Al_3Ni phase consumption and formation rate, giving rise to constant growth kinetics, while on the other hand, it leads to parabolic growth kinetics of the AlNi layer. This parabolic function implies that the AlNi growth dependency on the reaction has subsided.

The growth rate constant k is an exponential function of the temperature variable, cf. equation 4. Whereby Q is the activation energy for diffusion-limited growth and k_0 represents an independent factor of time and temperature and R= the global gas constant.

$$k = k_0 \exp(\frac{-Q}{RT}) \quad (4)$$

$$ln\, k = ln(k_0) - \frac{Q}{RT} \quad (5)$$

By combining equations (1) and (4), equation (6) is obtained as follows:

$$W = f(T,t,n) = k_0 t^n \exp(\frac{-Q}{RT}) \quad (6)$$

Defining the B parameter as equation (7), W is a function of temperature according to equation (8) (for constant values of n and t).

$$B = f(t,n) = k_0 t^n \quad (7)$$

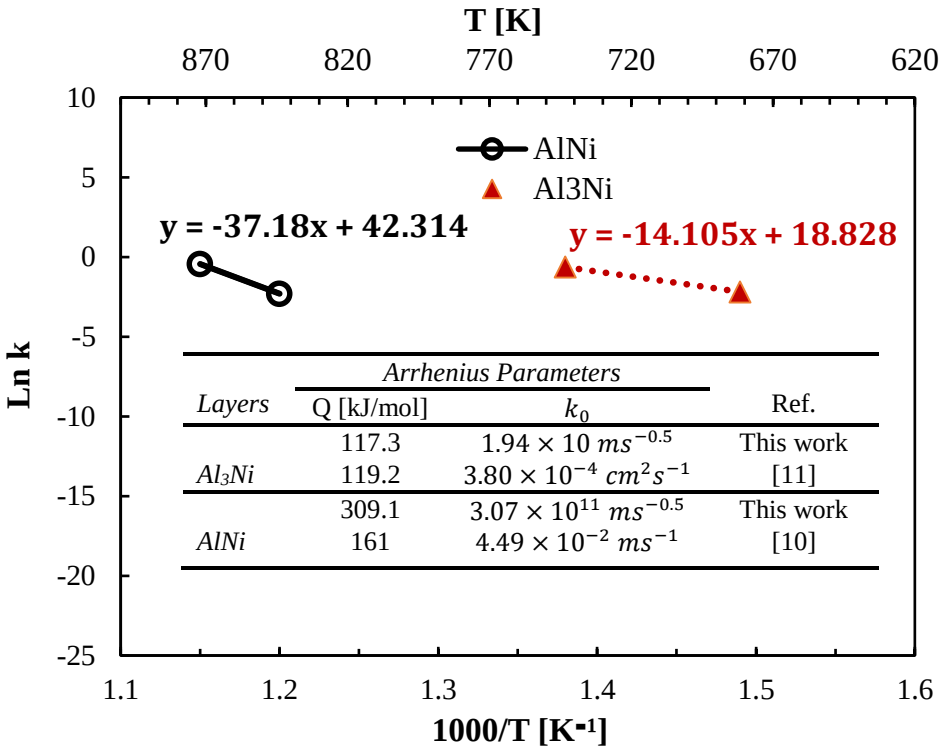
$$W = f(T) = B\exp(\frac{-Q}{RT}) \quad (8)$$

Table 3. B function according to n values.

Layer - T(℃)	n	B	$\frac{\partial W}{\partial t}$, growth rate	Considerable remarks
Al_3Ni - 563	-1	$\frac{k_0}{t}$	<0	Layer consumption
Al_3Ni - 525, 600	0	k_0	0	Growth depends on temperature, independent of time
Al_3Ni - 400, 450	0.5	$k_0 t^{0.5}$	>0	Parabolic kinetics
AlNi - 600				
AlNi - 563	1	$k_0 t$	>0	Linear kinetics
AlNi - 525	4	$k_0 t^4$	>0	Growth depends on interface reaction strongly

Based on the present values for the n variable, the B function appears in five forms which are listed in Table 3. In both layers, the dependency of B on the time is decreasing with temperature increase, independent of the function form and except at 600℃ for B_{Al_3Ni}. At 600℃, this dependency is higher owing to the presence of the thick and compact layer of AlNi, which gives rise to a deceleration of the supply of Ni atoms by the diffusion process in order to form the Al_3Ni phase.

The Q value is calculated, cf. Figure 4, under the condition that growth is controlled by diffusion (n=0.5). Hence, this calculation is possible for the Al_3Ni layer in the 400-450°C range and estimation for AlNi layer in the 563-600°C range with the least possible error. The estimation here obtained is far from the finding by Urrutia et al [10] because of the mixture of bulk and grain boundary (GB) diffusion for AlNi formation in the present work. This can be explained by the wave-like morphology of the Al_3Ni/AlNi interface as one might expect from GB diffusion, cf. Figure 5.



	Arrhenius Parameters		
Layers	Q [kJ/mol]	k_0	Ref.
	117.3	$1.94 \times 10\ ms^{-0.5}$	This work
Al_3Ni	119.2	$3.80 \times 10^{-4}\ cm^2s^{-1}$	[11]
	309.1	$3.07 \times 10^{11}\ ms^{-0.5}$	This work
AlNi	161	$4.49 \times 10^{-2}\ ms^{-1}$	[10]

Figure 4. ln k versus 1/T plot and the corresponding Arrhenius parameters.

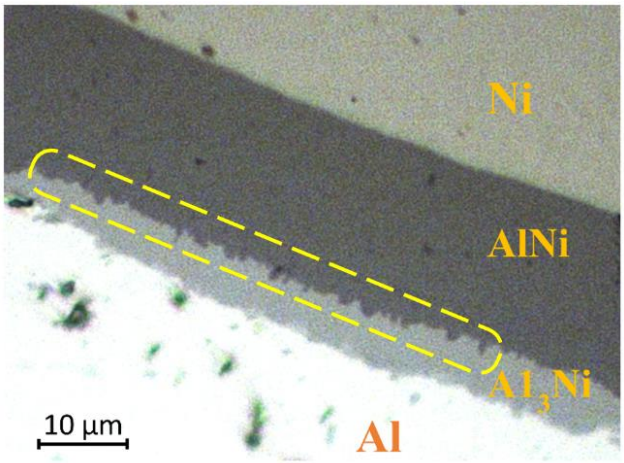


Figure 5. A typical wave-like interface of the Al_3Ni/AlNi in TD section (the sample was annealed at 600 for 4 h).

The overall growth assessment of intermetallic layers reveals an exponential trend as a function of temperatures, cf. Figure 6, indicating bulk diffusion-controlled growth of layers according to the Arrhenius model. Further, diffusion acceleration via base metals grain boundaries does not play a significant role during layers growth because the cold rolled grains of the base metals have already recrystallized and grown in the first stages of the annealing. After the annealing, Al and Ni grains exhibited the equivalent diameter of 60 and 102 µm from 2.3 and 50 µm in the cold roll-bonded stage, respectively.

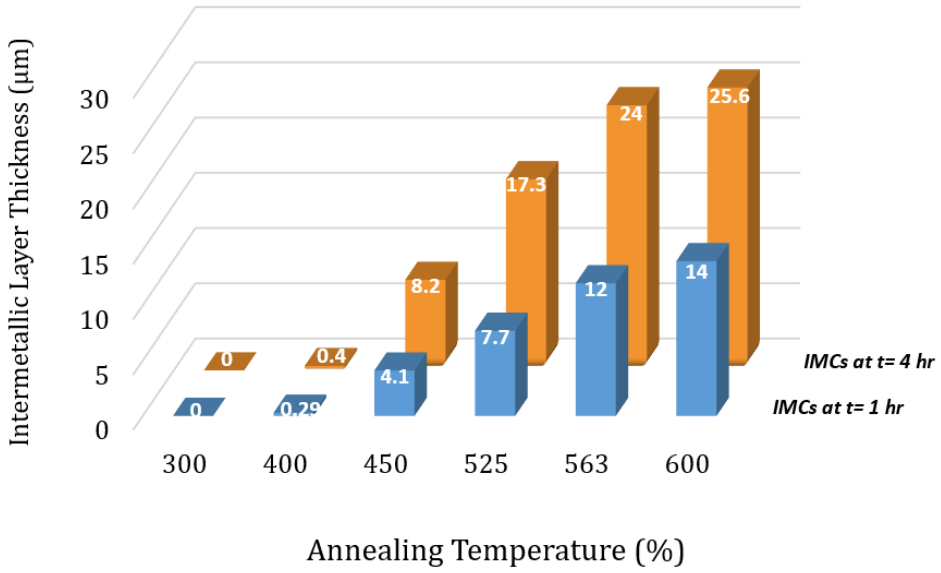


Figure 6. The overall Int. Met. layers thickness vs. annealing temperature during 1 and 4 hours.

4. Conclusion

An Al-AlNi-Ni laminate composite is relatively obtainable by annealing above 560°C longer than 4 h. In the term of growth kinetics and based on the overall assessment, intermetallic layers growth obeys Arrhenius model which indicates bulk diffusion controlled growth. However, internal layers exhibit different behaviors of sequential growth, concurrent growth and layer decreasing through decomposition. Up to 450°C, only Al_3Ni layer was formed and followed the second stage of a two-stage growth process. By emerging AlNi compound at higher temperatures, Al_3Ni growth behavior changes to consumption. The AlNi layer formation was controlled by a mixture of bulk and grain boundary diffusion while bulk diffusion was the only mechanism which controls the growth of Al_3Ni with activation energy similar to the previous studies.

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