Since the Schubert cycles form an integral basis for $H_*(G(k,n),\mathbb{Z})$, it follows either by Poincare duality and the fact that analytic cycles intersect positively or by direct computation that

$$\#(\sigma_a \cdot \sigma_{n-k-a_k,\cdots n-k-a_1}) = 1.$$

Γ By P 62, analytic cycles intersect positively.

Consider a linear functional on $H_{2k(n-k)-2\Sigma b_i}(G(k,n),\mathbb{Z})$ defined as follows:

$L(\sigma_b) = 1$ if $b_{k-i+1} = n-k-a_i$ for all $i = 1 \cdots k$.
$L(\sigma_b) = 0$ if $b_{k-i+1} \neq n-k-a_i$ for some i
where $\{a_1 \cdots a_k\}$ given.

$\Rightarrow$ By Poincare duality (P53), L is expressible as intersection with some class $\alpha \in H_{2\Sigma b_i}(G(k,n),\mathbb{Z})$.
$\Rightarrow$ $\alpha = \Sigma\, x_a \sigma_a$, $\sigma_a \in H_{2\Sigma b_i}(G(k,n),\mathbb{Z})$.
$x_a \in \mathbb{Z}$
As we know from the above, $\#(\sigma_a \cdot \sigma_b) = 0$ unless $b_{k-i+1} = n-k-a_i$ i.e. $a_i = n-k-b_{k-i+1}$ for all i. $\Rightarrow$ $x_a = 0$ unless $\{a_i\} = a$
since $L(\sigma_b) = \#(\alpha \cdot \sigma_b)$
Furthermore, $x_a = 1$ if $a = \{a_1 \cdots a_k\}$
, and $L(\sigma_b) = \#(\sigma_a \cdot \sigma_b) = 1$
Actually, we don't make clear why $\#(\sigma_a \cdot \sigma_b) = 0$
even if $a_i = n-k-b_{k-i+1}$, for all i.
Suppose $\#(\sigma_a \cdot \sigma_b) = 0$ even in case $a_i = n-k-b_{k-i+1}$